Understanding Interfacial Structures of Ultrathin Self-Assembled Nafion®

John Fischer

Introduction

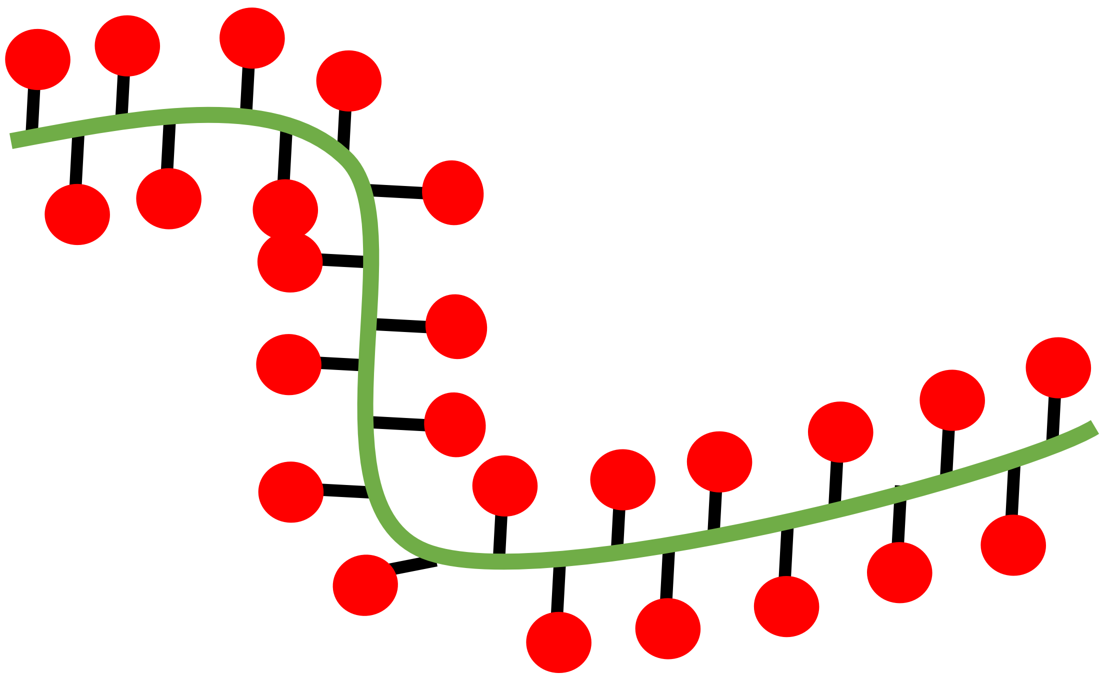
Understand interface structure of Nafion® with Both electrode particles and additive particles

Why are fuel cells important?

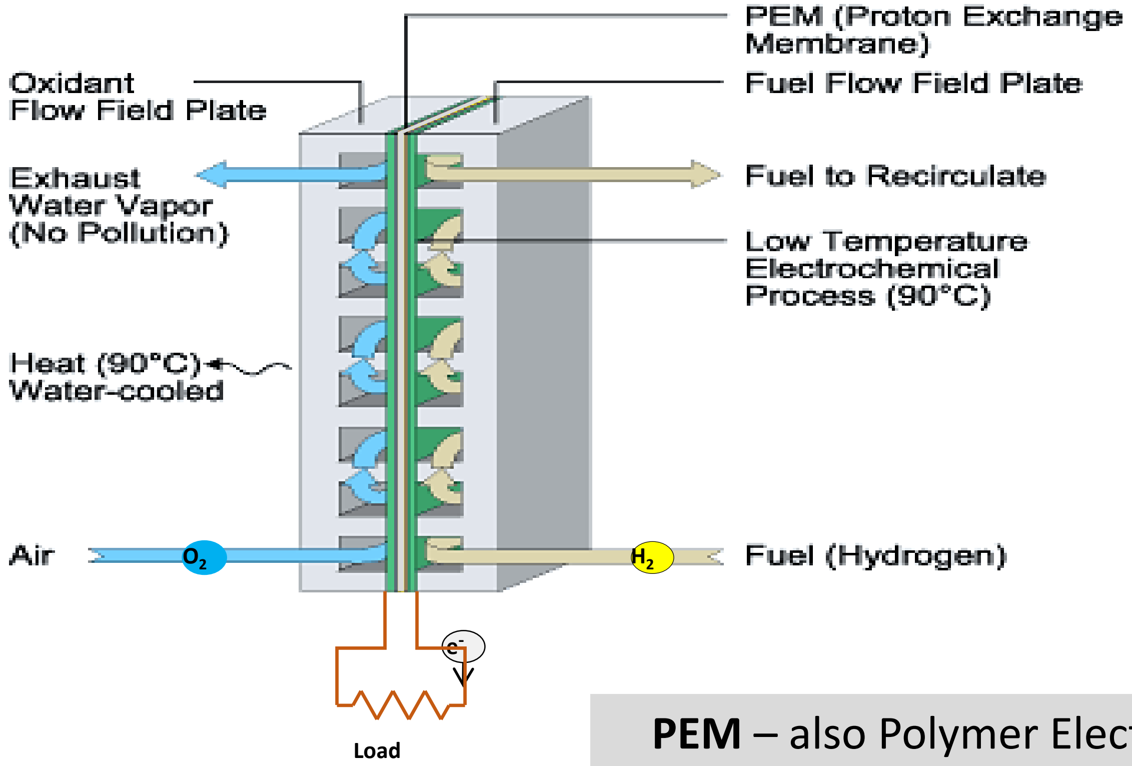
- Clean Energy
- Vast Applications
- Green alternative to batteries and gasoline based generators

OUTLINE

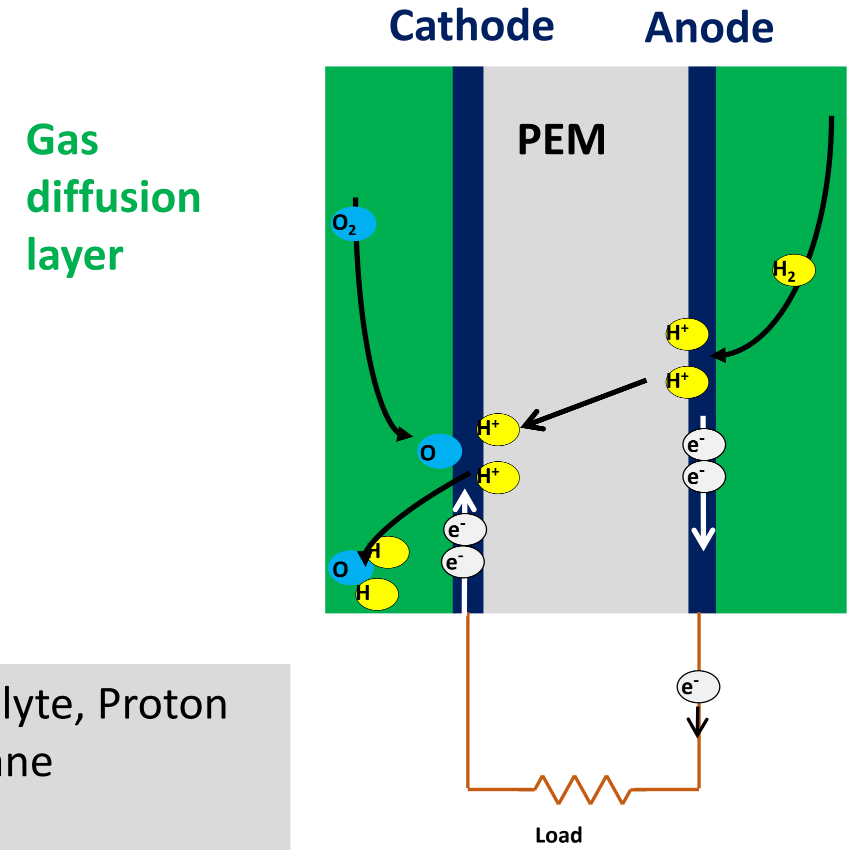
- Fuel Cell Overview
- Nafion® Coating Methods
- Literature
- Testing Methods
- Results
- Conclusions



PEM Fuel Cell



Membrane Electrode Assembly

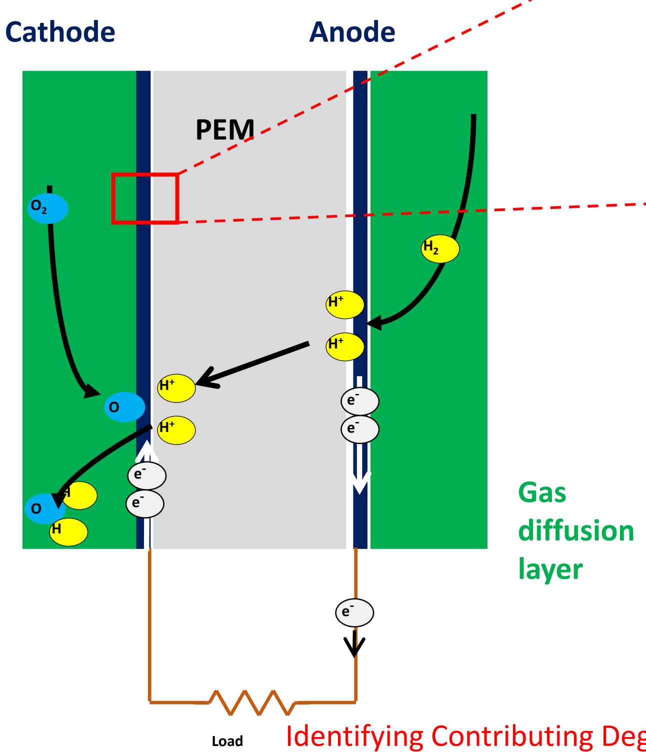


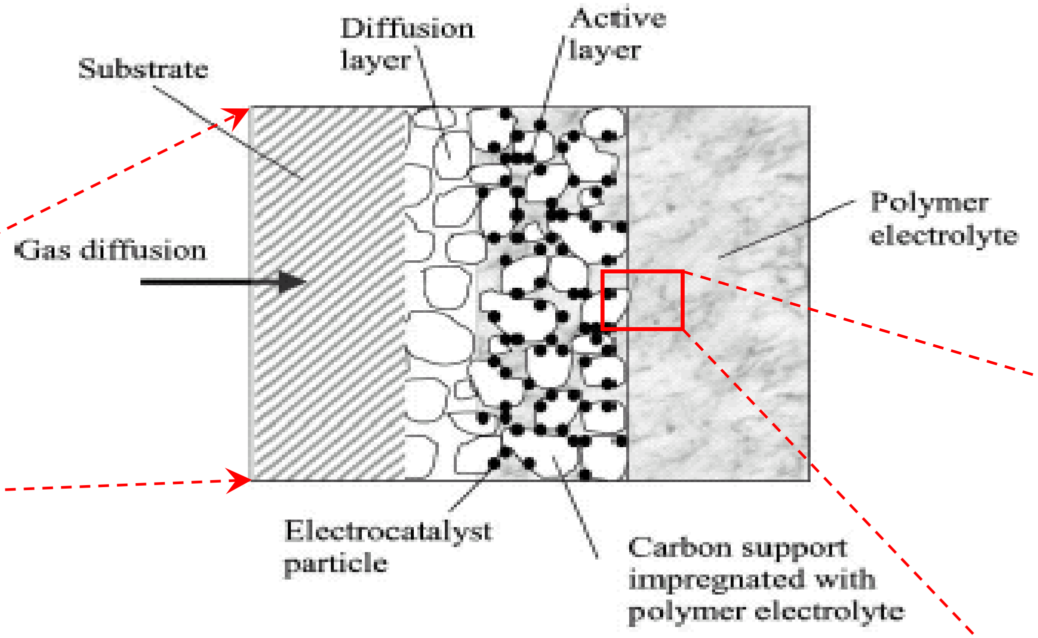
PEM – also Polymer Electrolyte, Proton Exchange Membrane

Passes H^+ ions

Impervious to e^-, H_2, O_2

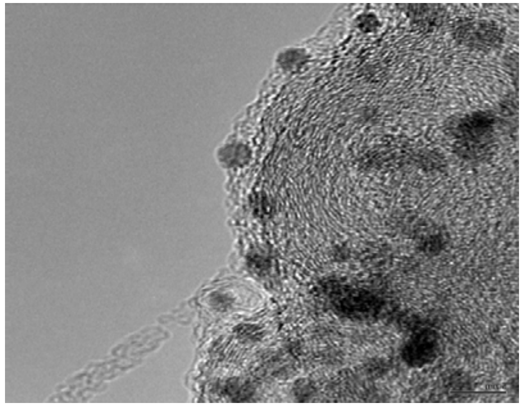
Membrane Electrode Assembly





Three Phase Region

(where gasses electrode and PEM come together to allow the electrochemical reaction)



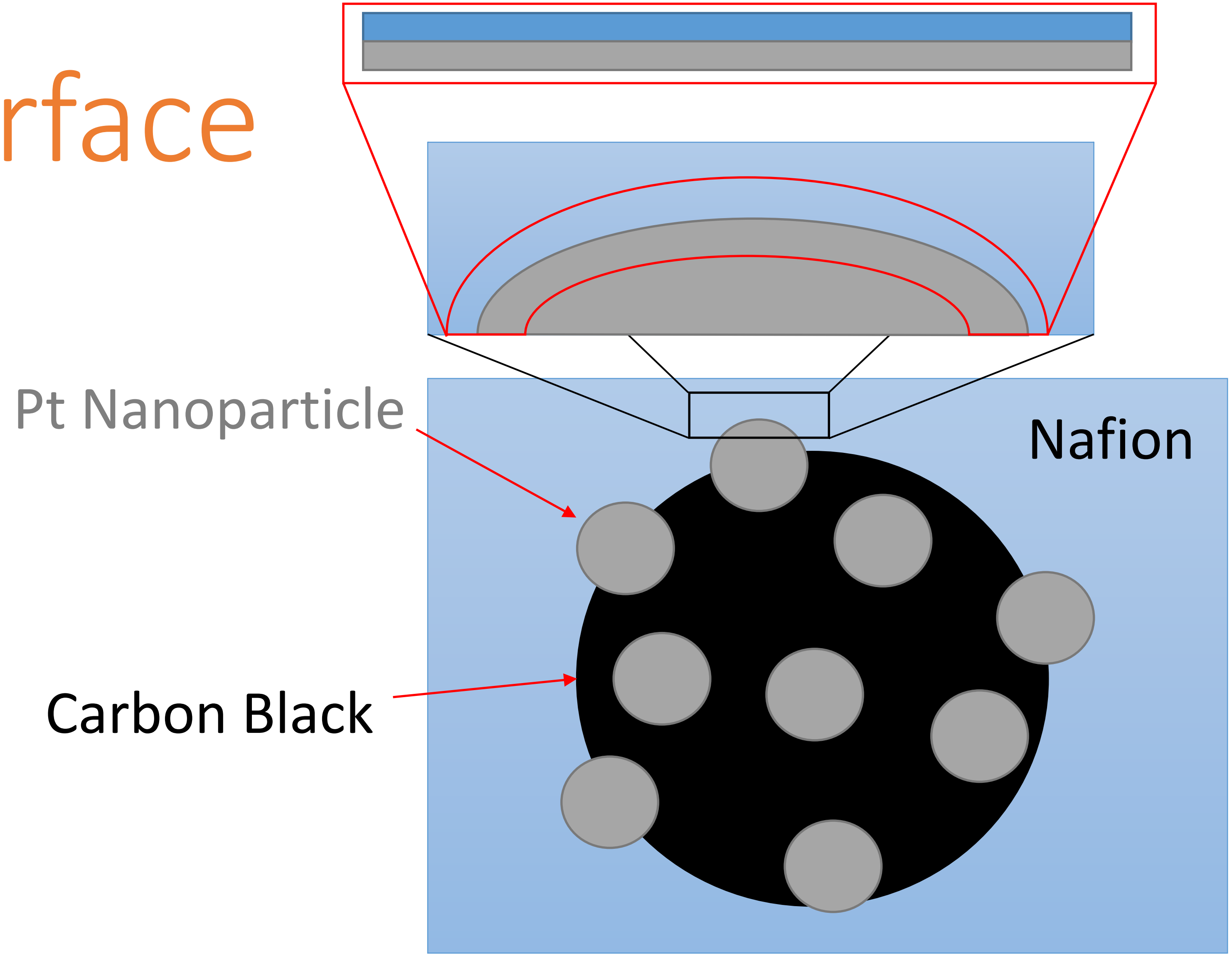
Identifying Contributing Degradation Phenomena in PEM Membrane Electrode Assemblies Via Electron Microscopy
K. L. More, R. Borup, and K. S. Reeves *ECS Transactions* **3(1)** pp. 717-733 2006

Idealized Interface

Why do we want to do this?

- Allows interface nanostructure studies via Neutron Reflectometry

Self Assembled Nafion® is from a commercial dispersion diluted in Isopropyl Alcohol



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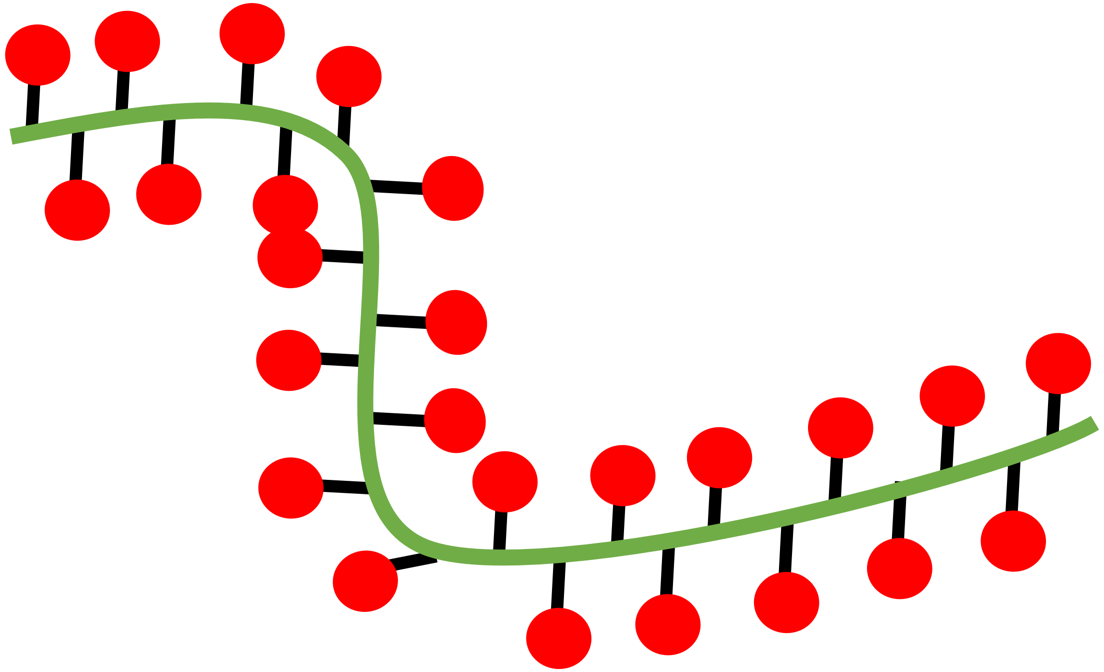


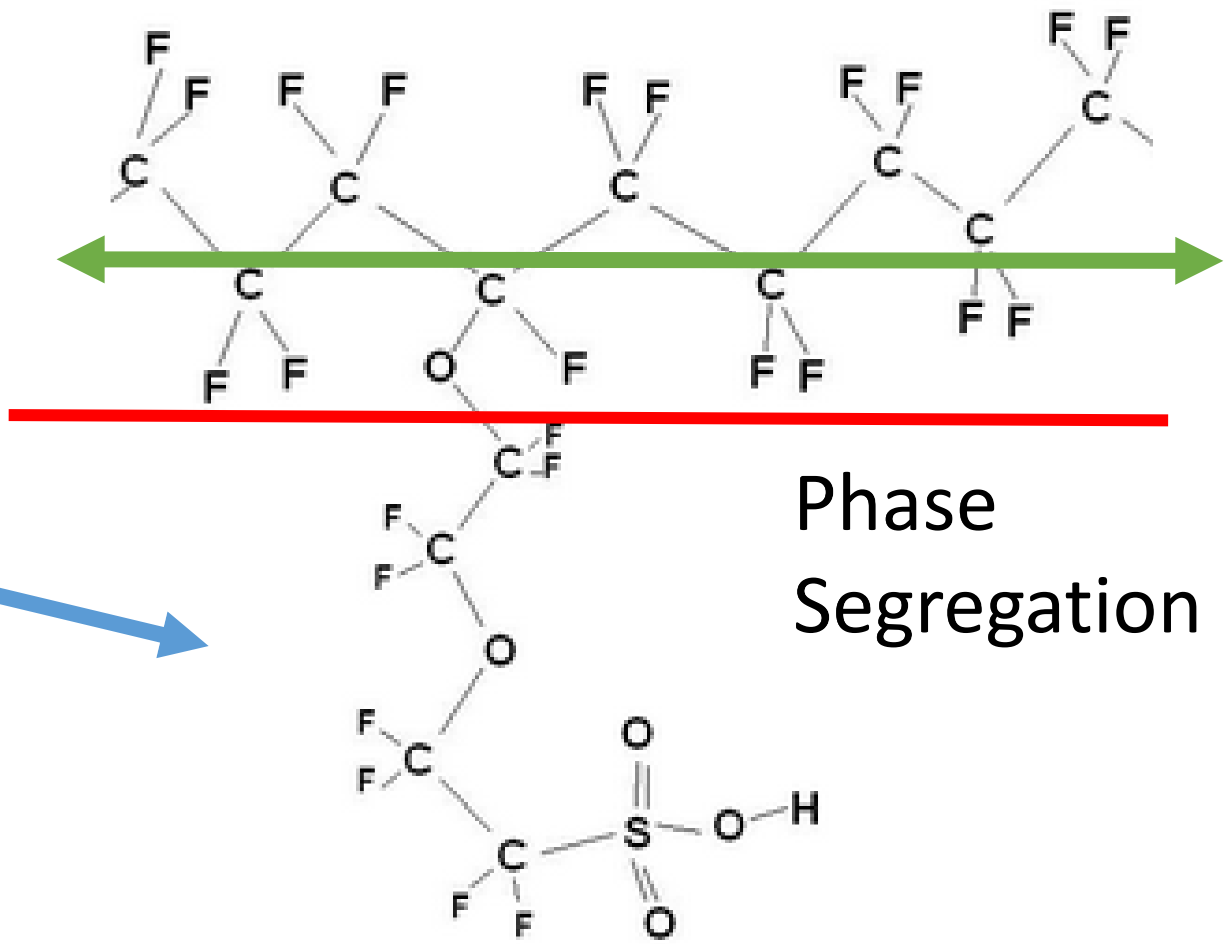
Nafion®

Teflon Backbone

- Provides Structure
- Impervious to e^-, H_2, O_2
- Hydrophobic

Sulfonate Side Chains

- Hydrophilic
- Absorbs H_2O
- Passes H^+ ions



Some interesting properties to investigate:

- Swelling when hydrated
- Rate of swelling with relative humidity
- Lamellar structure

http://www.doitpoms.ac.uk/tlplib/fuel-cells/pem_membrane.php

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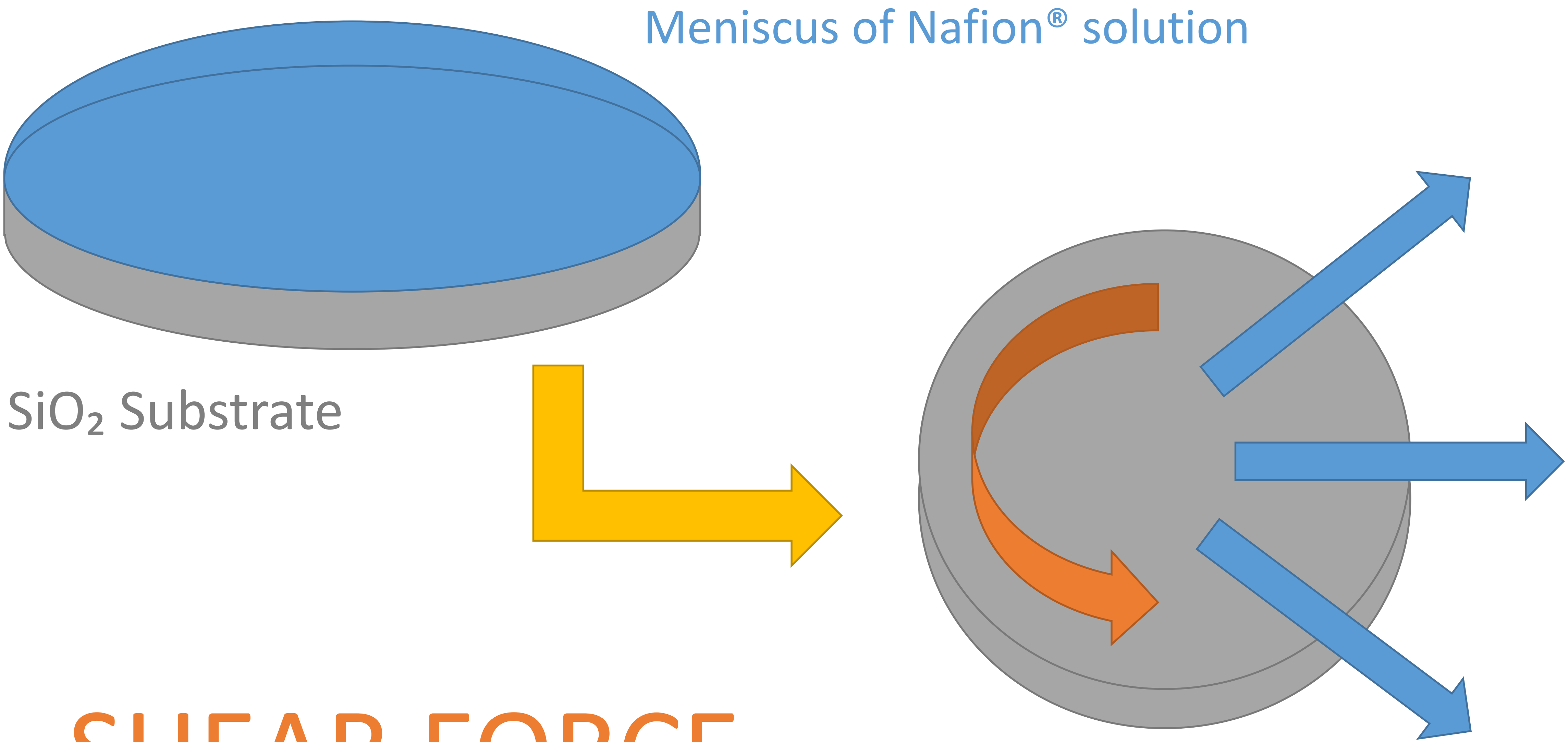
NIST

What is Spin Casting compared to Self-Assembly?



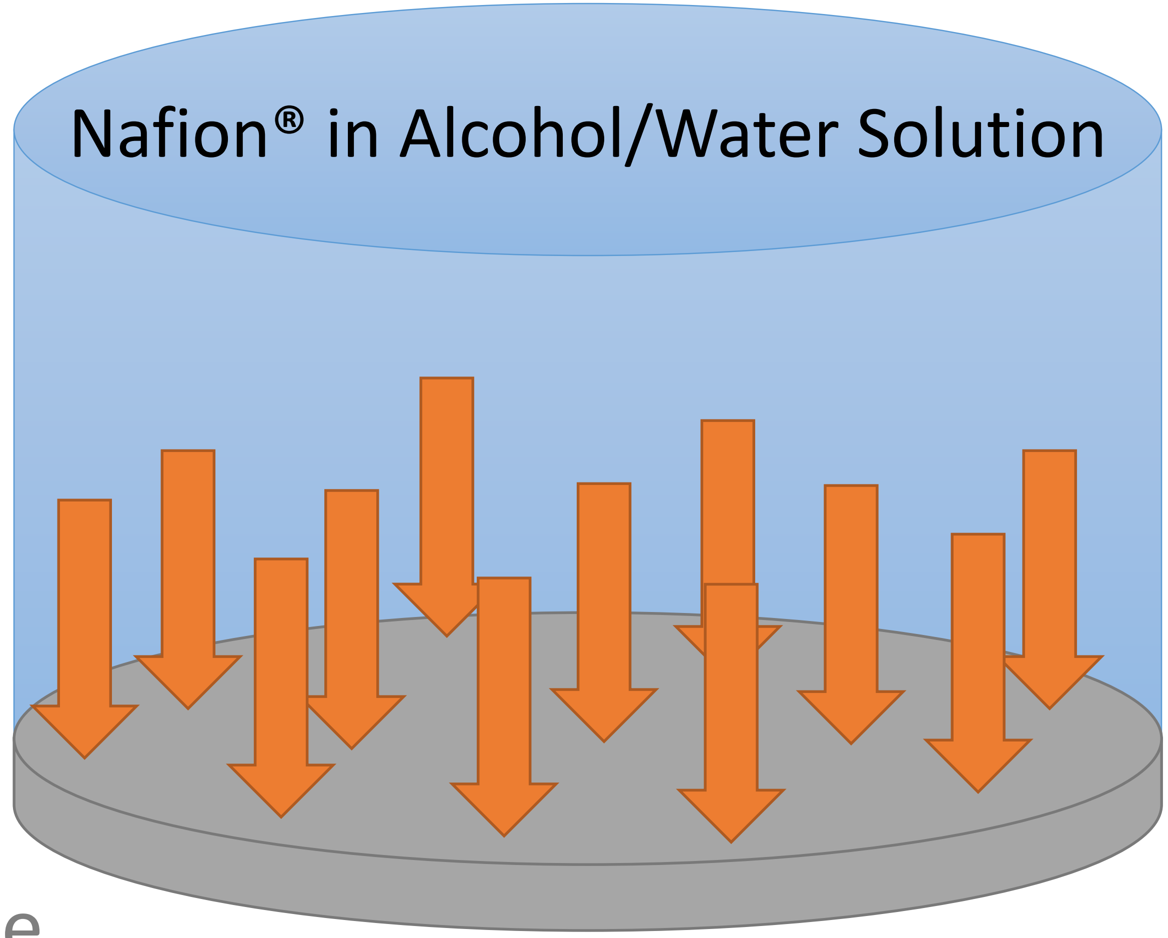
SHEAR FORCE

Nafion® Self-Assembly

- Make Ultrathin films consistently
- Establish singular procedure for future reference
- Need to be smooth, uniform, suitable for NR/XRR
- Clearly define what "Self-Assembly" is for Nafion

- MOST IMPORTANTLY: EASILY REPRODUCEABLE

Self-Assembly Method



18 HOURS

SiO_2 Substrate

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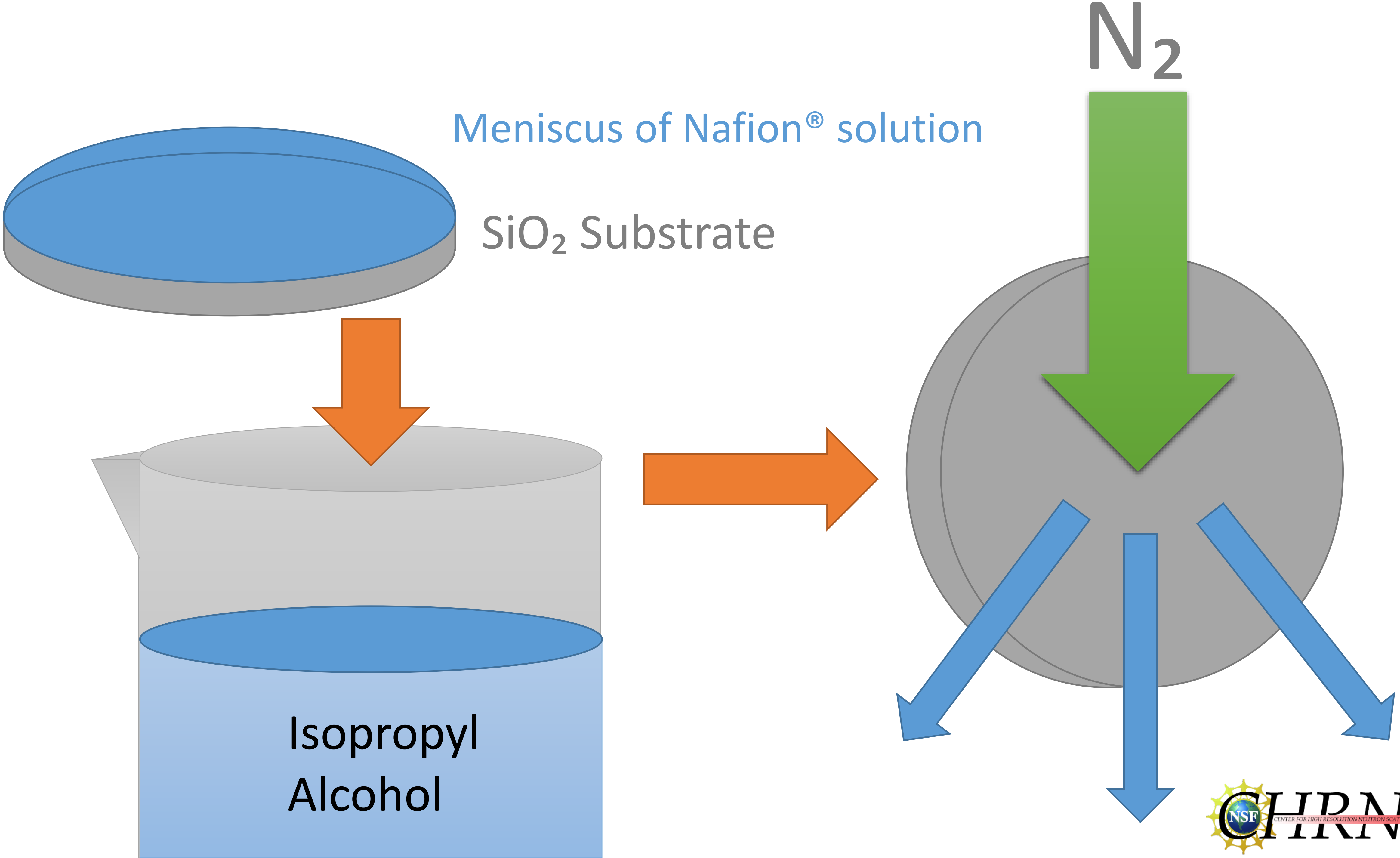
N_2
Meniscus of Nafion® solution
SiO_2 Substrate
Isopropyl
Alcohol

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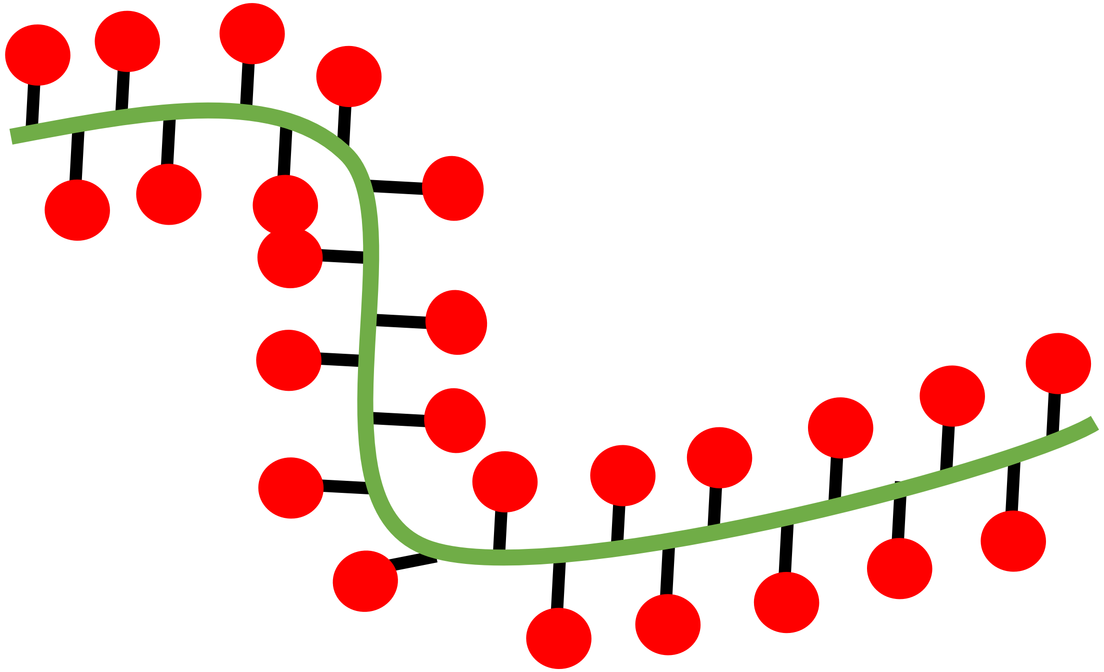
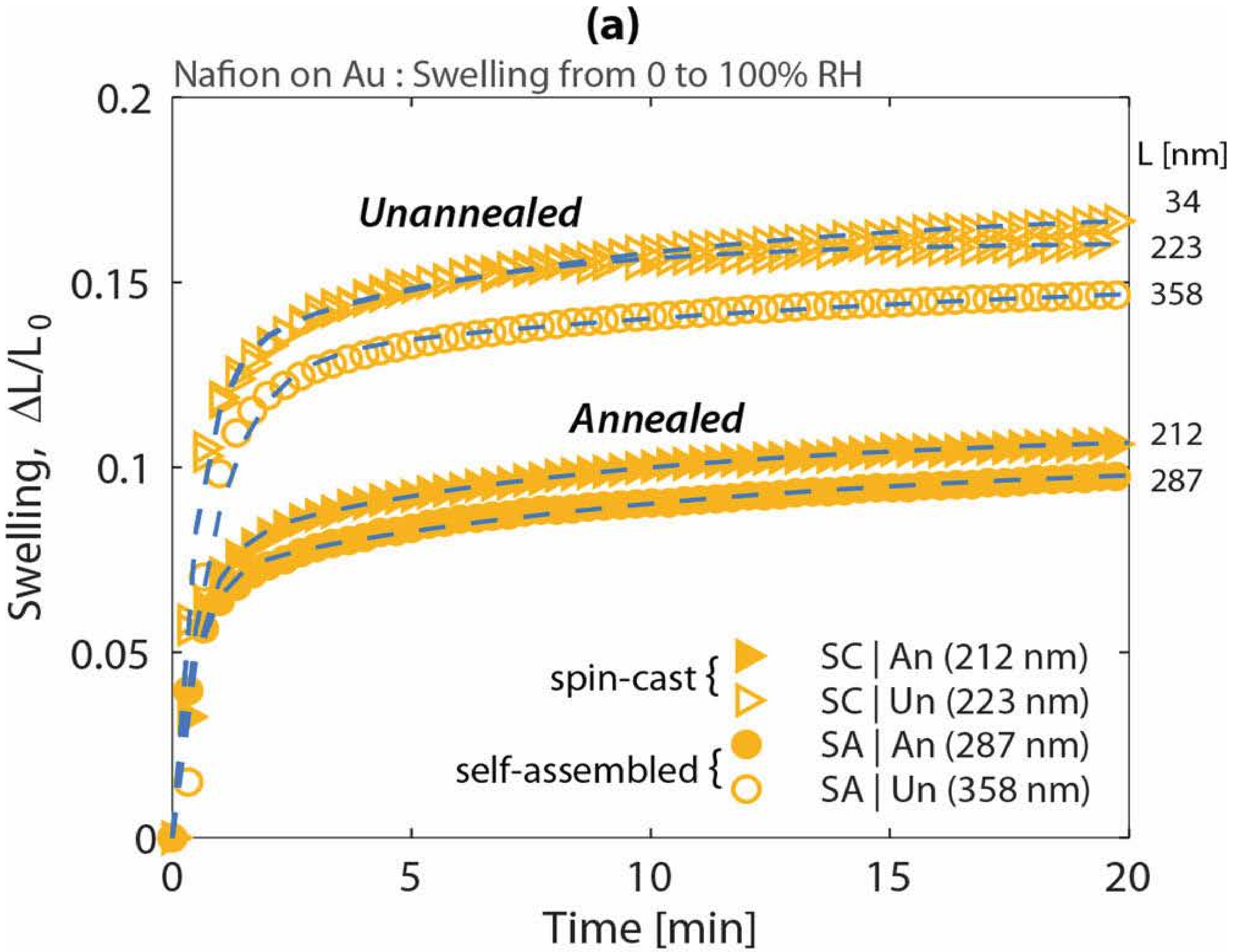


Kusoglu et. al

- Slight differences, yet present
- Differences between Self-Assembled (SA) and Spin Cast (SC) in absorption, swelling, and GISAXS intensity



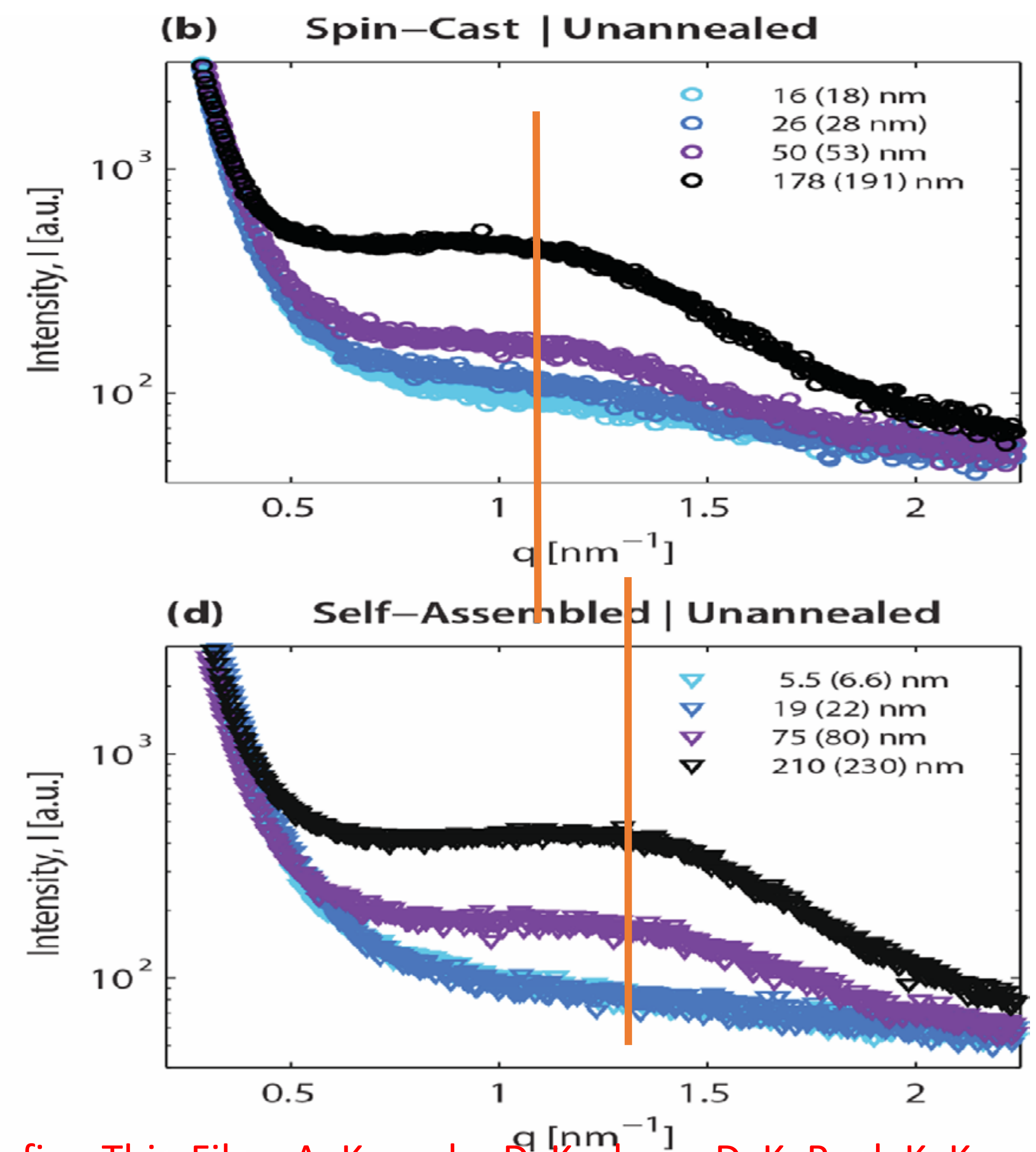
Impact of Substrate and Processing on Confinement of Nafion Thin Films
A. Kusoglu, D. Kushner, D. K. Paul, K. Karan, M. A. Hickner, and A. Z. Weber
Adv. Funct. Mater. 24, pp. 4763-4774 2014

Parallel line cuts from GISAXS intensity profiles

Offset of Ionomer peaks

Broadening of ionic domain peaks with annealing

Noticeable differences between Self-Assembled and Spin-Cast



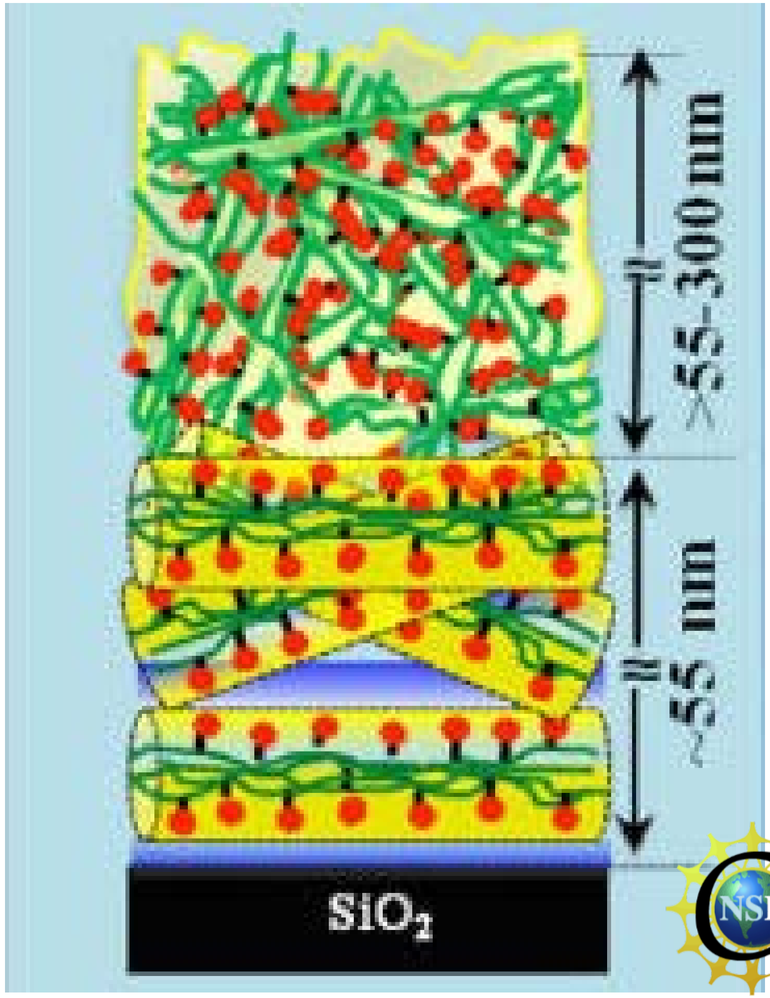
Impact of Substrate and Processing on Confinement of Nafion Thin Films A. Kusoglu, D. Kushner, D. K. Paul, K. Karan, M. A. Hickner, and A. Z. Weber *Adv. Funct. Mater.* 24, pp. 4763-4774 2014 + supporting Info

The question is, are the differences…

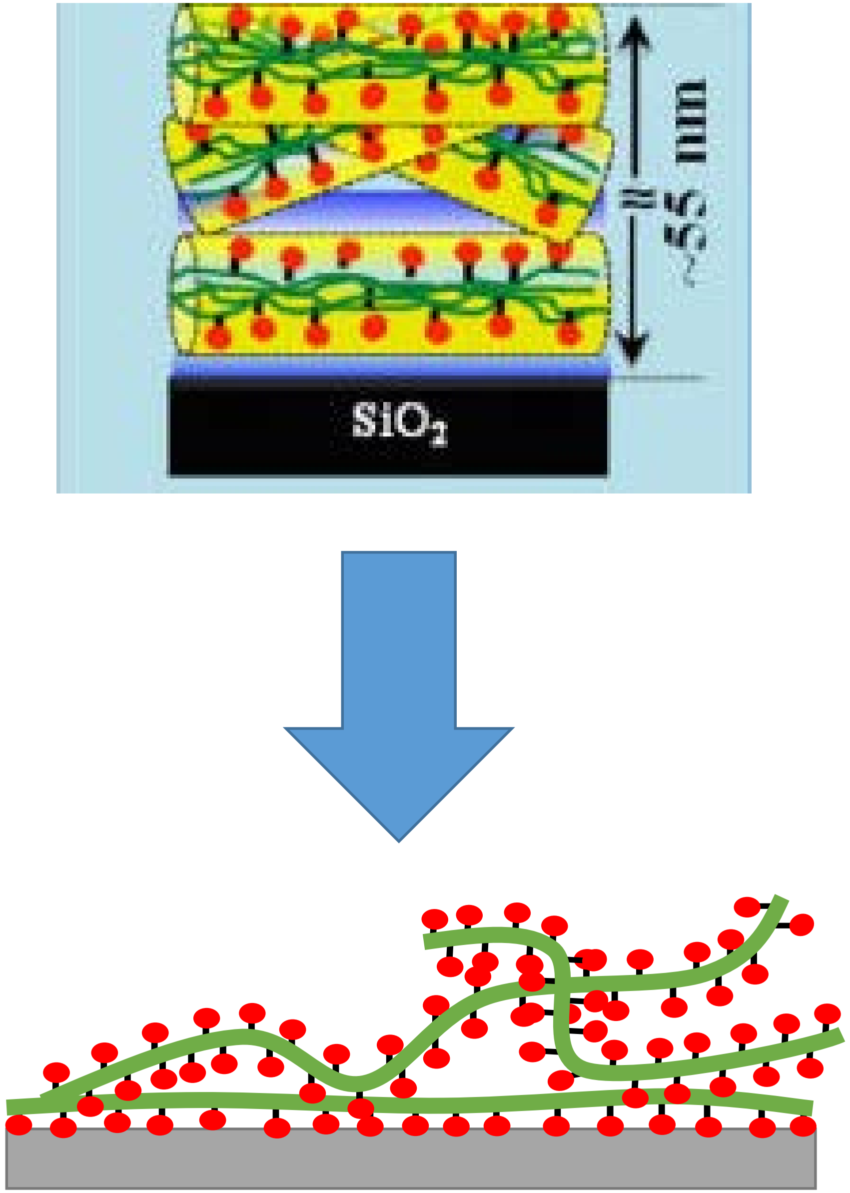
in the bulk-like
layer due to the shear,

or induced by interfacial forces
due to the different process?

Or Both?



Characteristics of Self-Assembled Ultrathin Nafion Films D. K. Paul, K. Karan, A. Docoslis, J. B. Giorgi, and J. Pearce *Macromolecules* **46** pp. 3461-3475 2013



Goals

1. Use reflectometry to analyze the polymer interface structures of SA Nafion®

2. Understand mechanism of film growth in SA Nafion® thin films

3. Develop a reproducible procedure for self-adsorbed Nafion® to establish SA films as a reliable model system for study of the substrate interface region of Nafion®.

Characteristics of Self-Assembled Ultrathin Nafion Films D. K. Paul, K. Karan, A. Docoslis, J. B. Giorgi, and J. Pearce *Macromolecules* **46** pp. 3461-3475 2013

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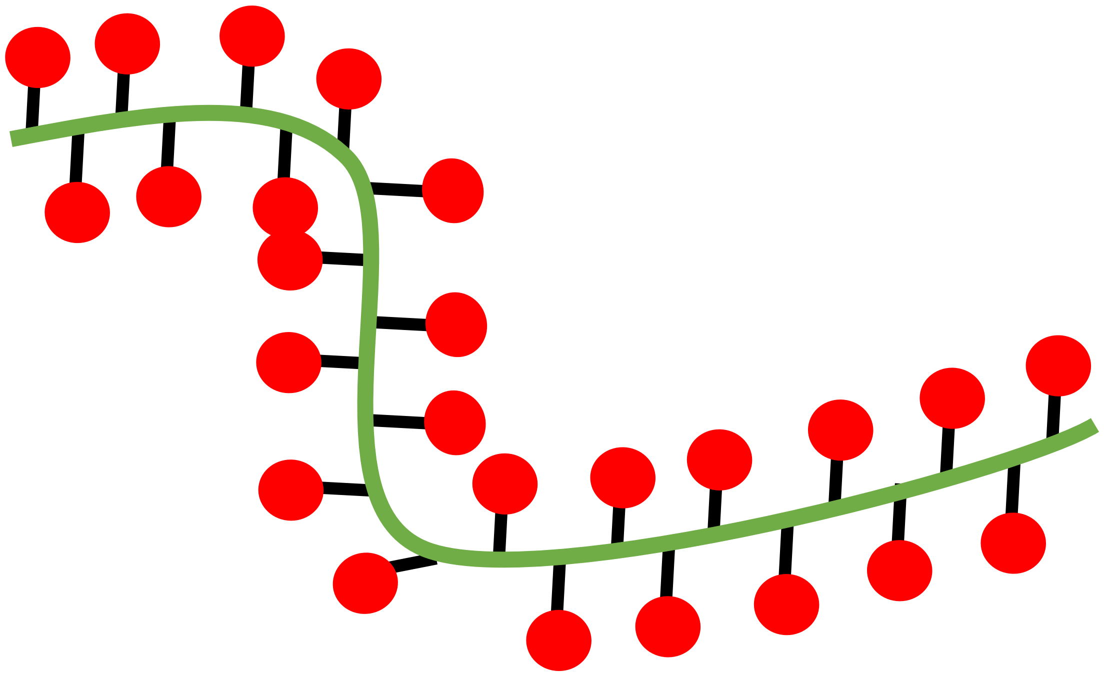

Testing

Uniformity and thicknesses explored at NIST using:

Variable Angle Spectroscopic Ellipsometry
X-Ray Reflectivity

And Mass/Thickness measured at Colorado School of Mines using:

Quartz Crystal Microbalance

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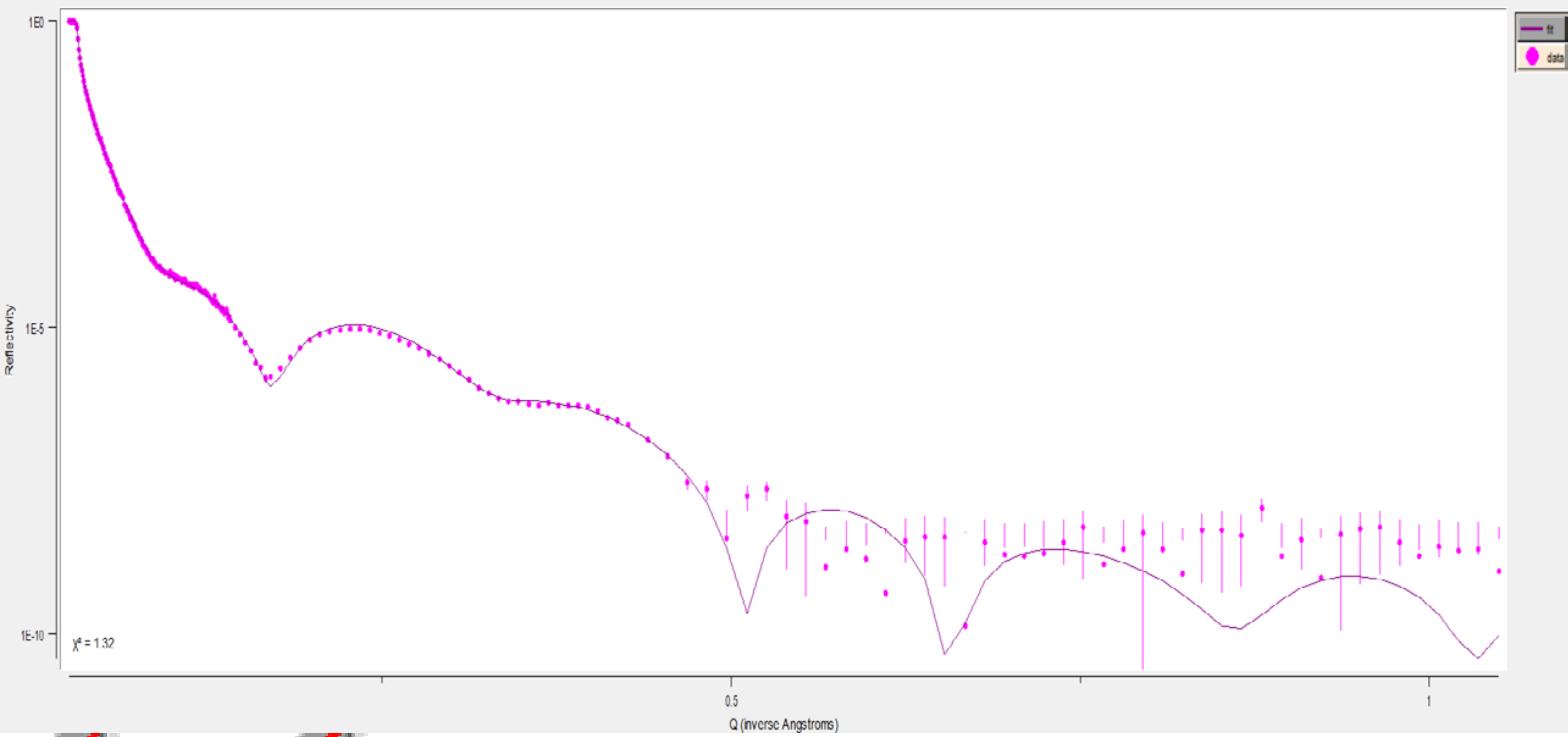
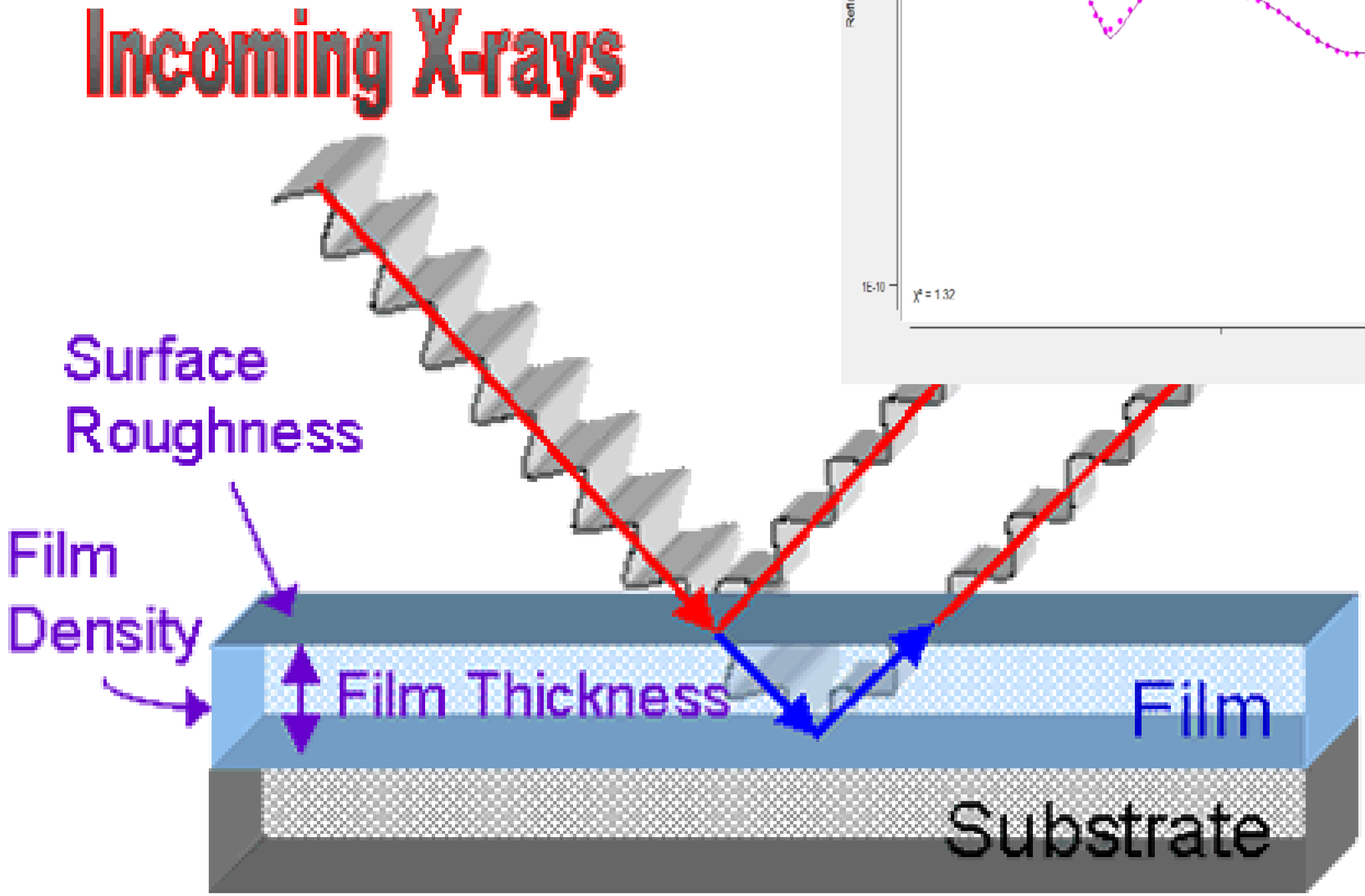
X-RAY Reflectivity





http://physics.valpo.edu/staff/arichter/XRR.htm

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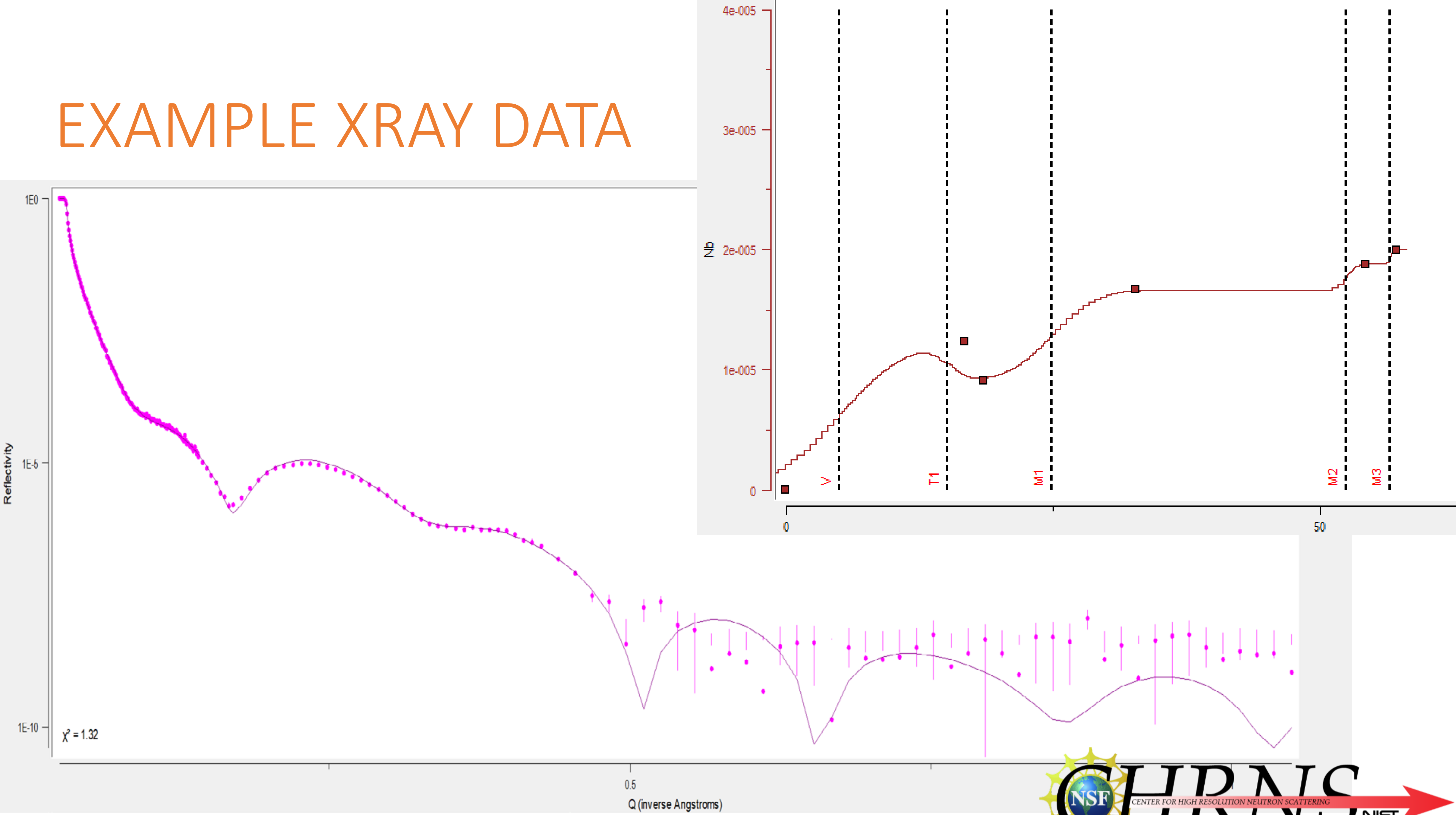
EXAMPLE XRAY DATA



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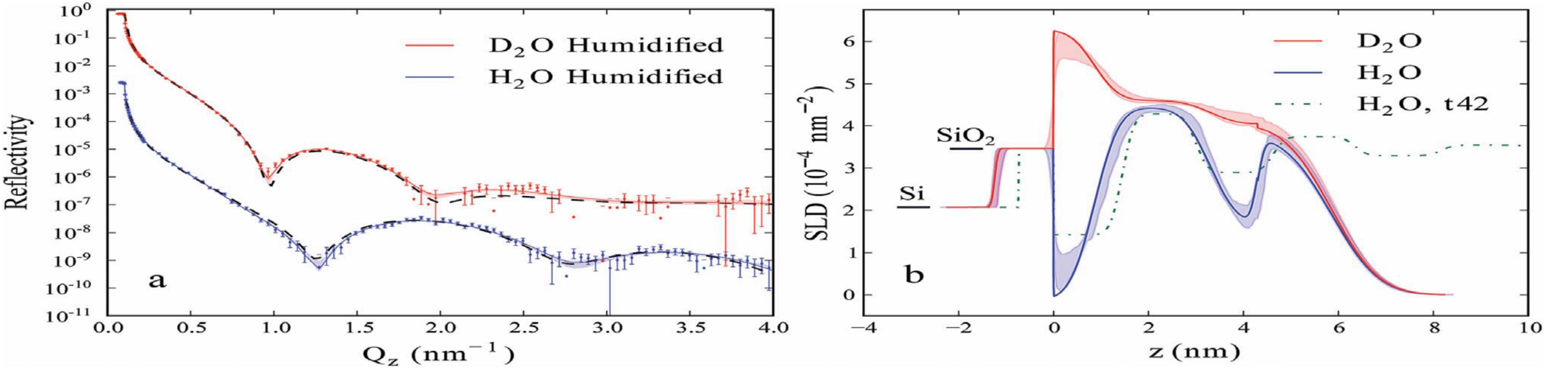
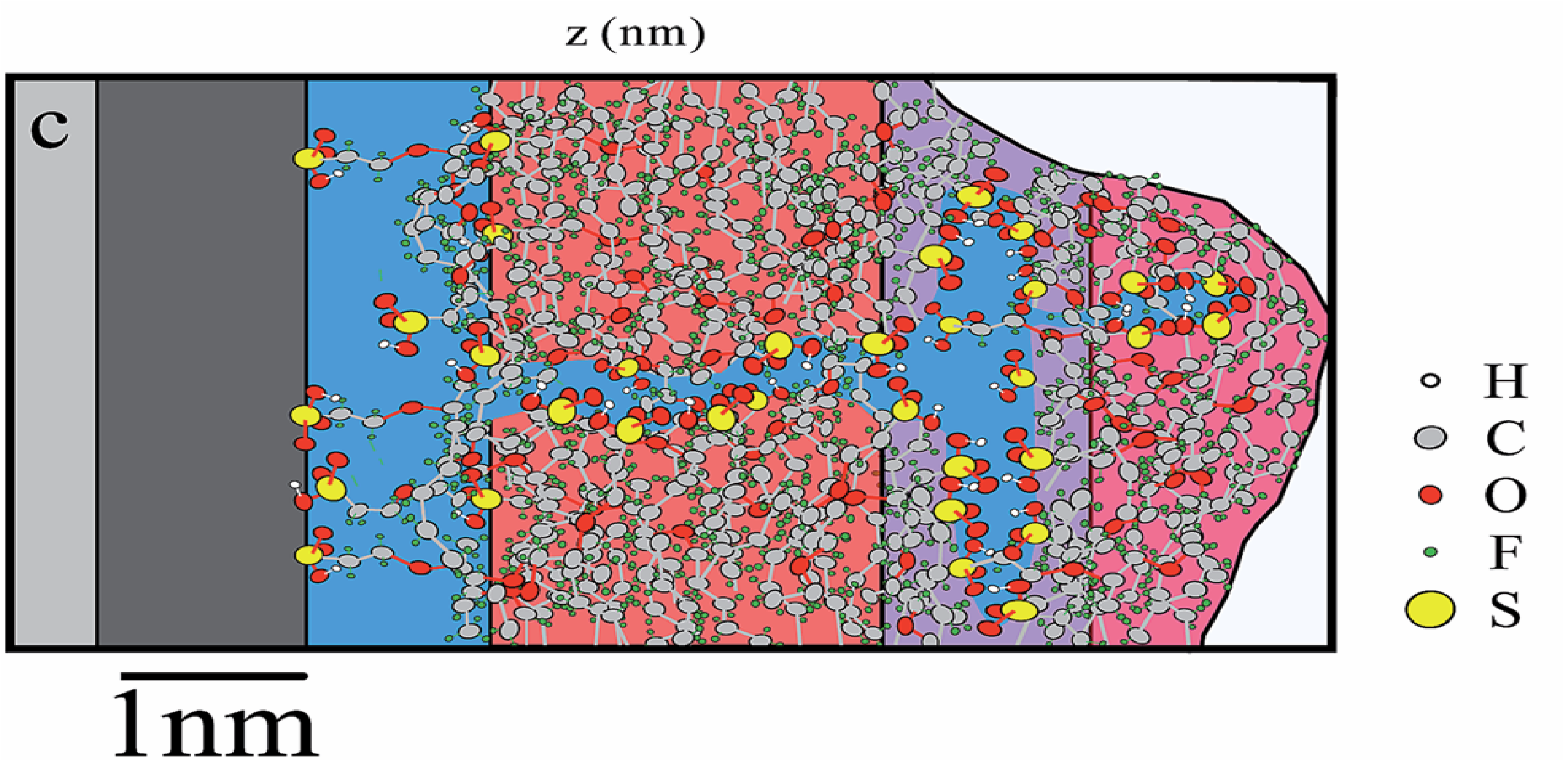
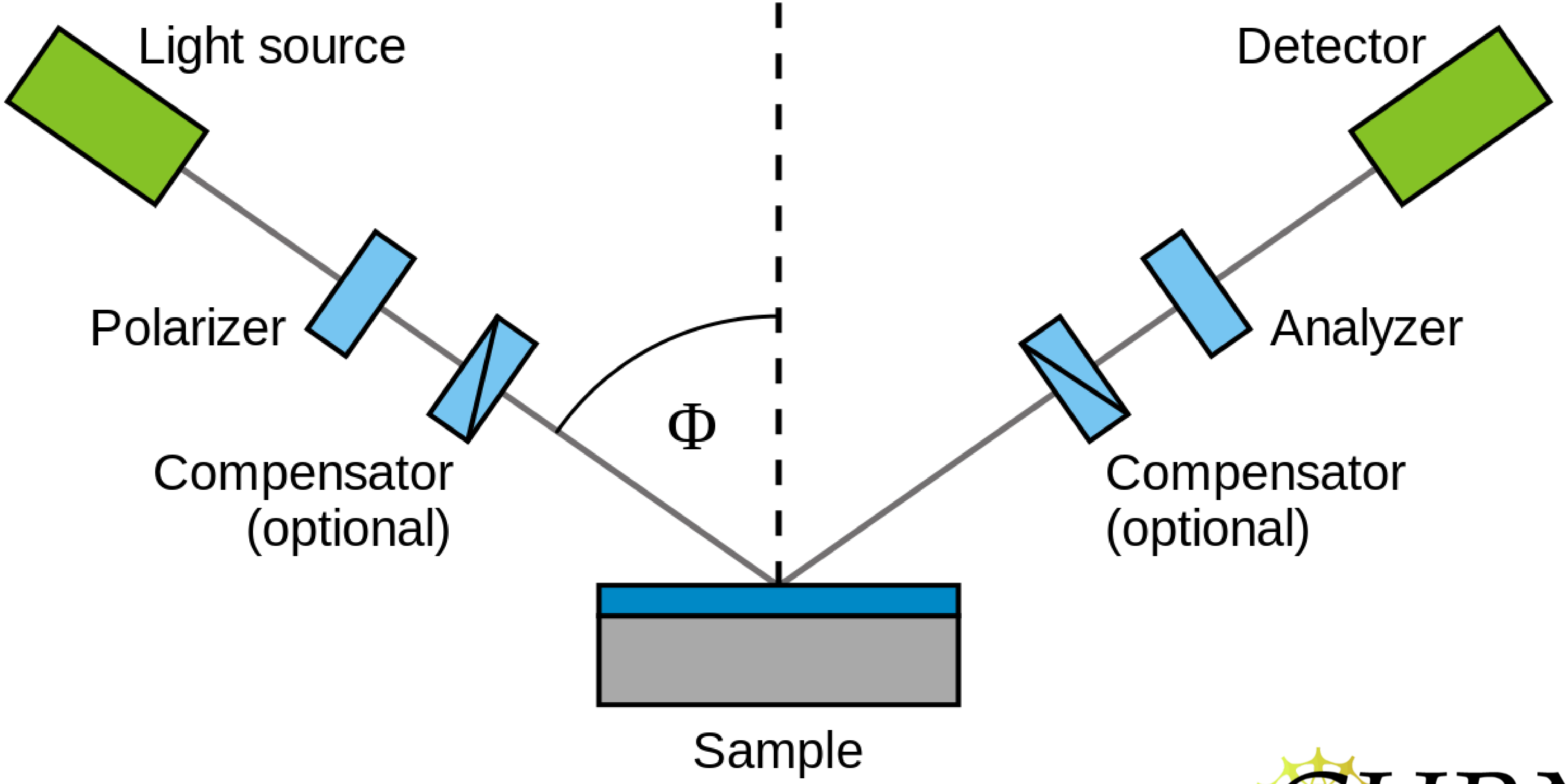


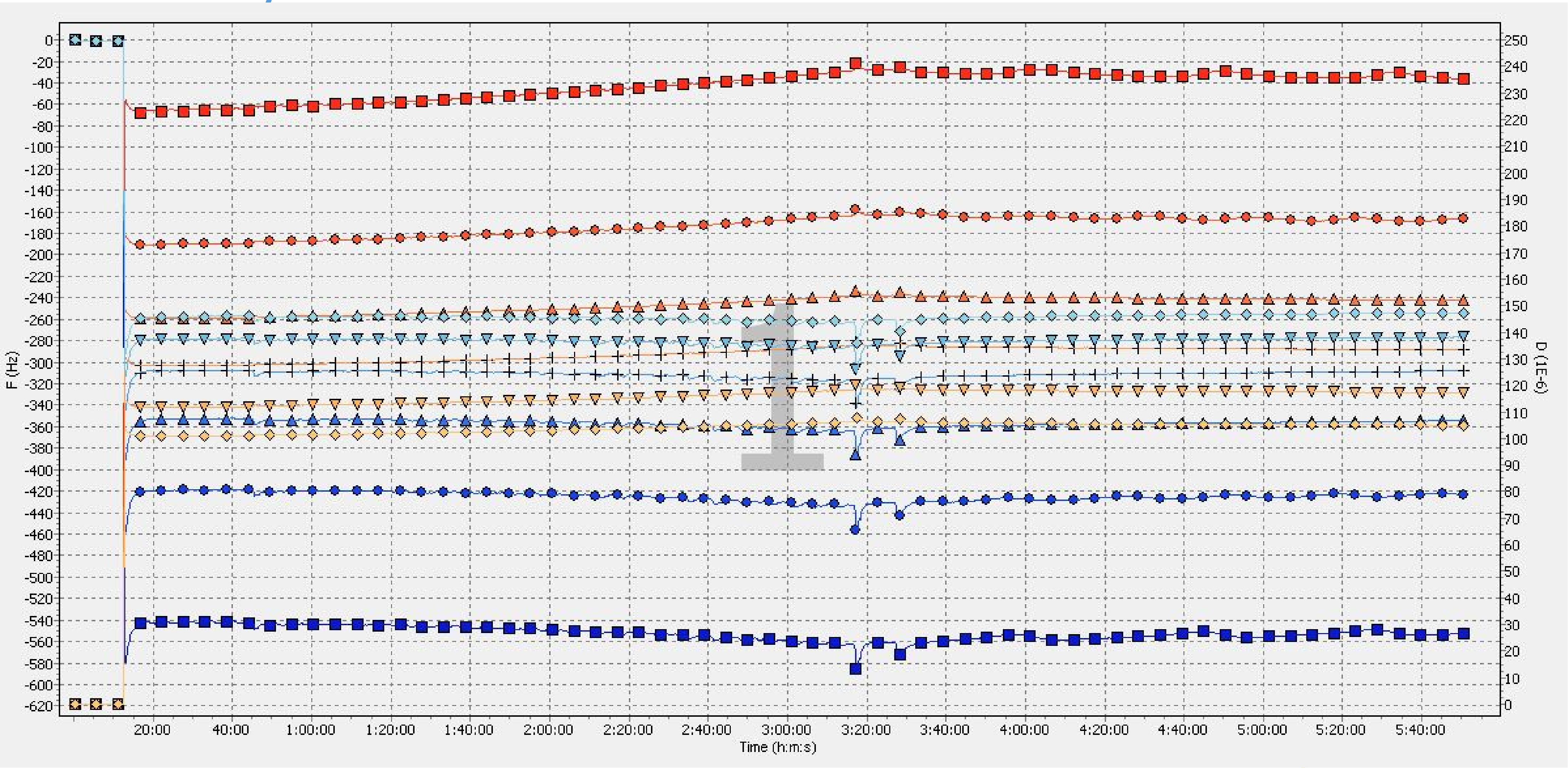


Phase segregation of sulfonate groups in Nafion interface lamellae, quantified via neutron reflectometry fitting techniques for multi-layered structures S. C. DeCaluwe, P. A. Kienzle, P. Bhargava, A. M. Baker, and J. A. Dura *Soft Matter* **10** pp. 5763-5776 2014

ELLIPSOMETRY



Quartz Crystal Microbalance



Frequency

Time

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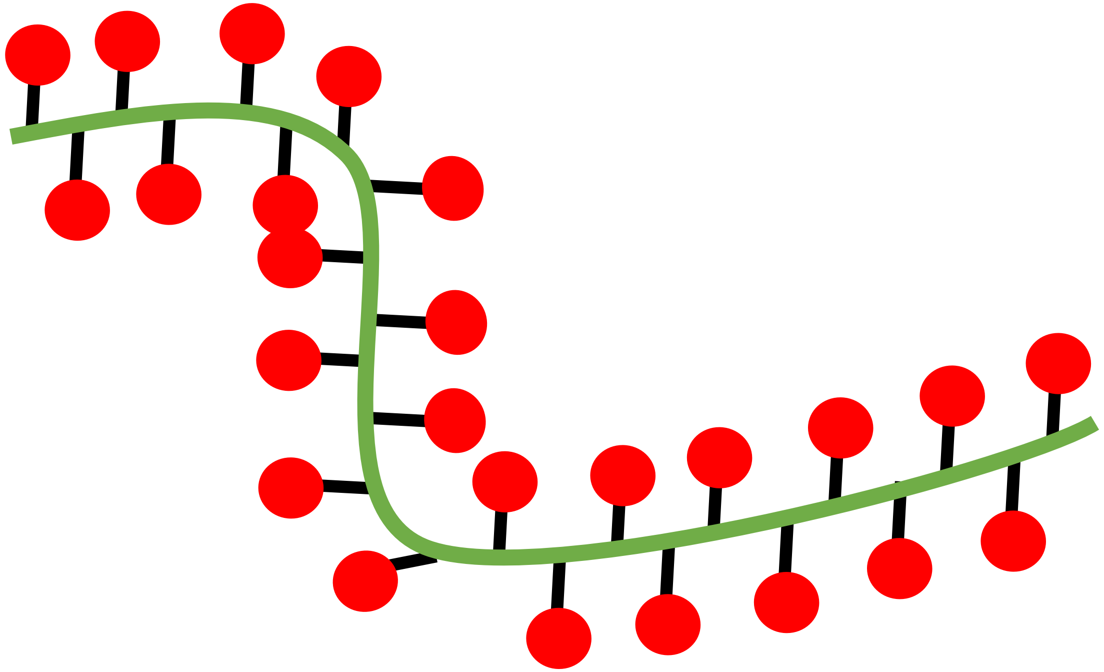
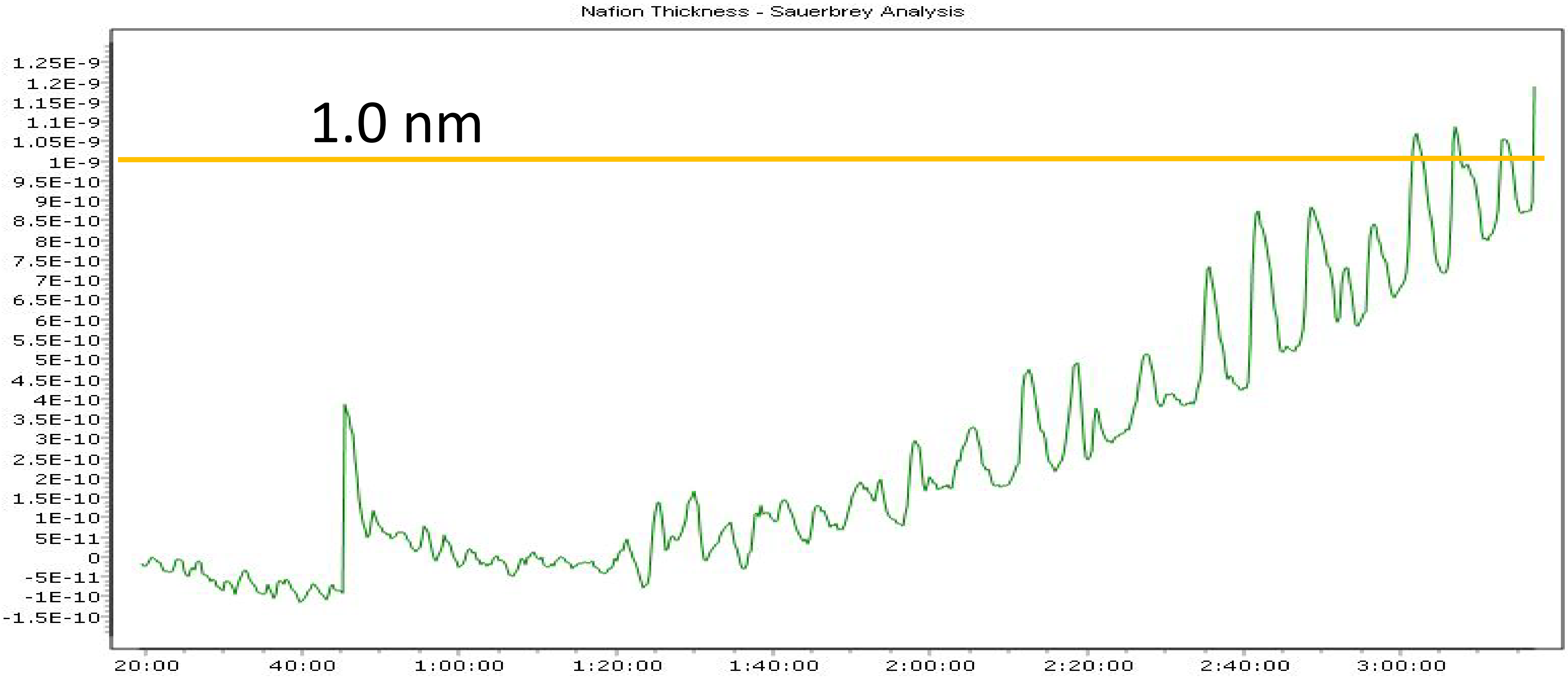


Quartz Crystal Microbalance Data (in solution)



Thickness (m) vs. Time

NIST Samples

Sample Name	Thickness (nm)	Method/Notes	Uniformity
SA001	2 (average)	67 hour soak, 7 dips	unknown
SA002	0.7 - 7	18 hour soak, 7 dips	best
SA003	4 (average)	18 hour soak, 5 dips	unknown
SA004	Unknown	18 hour soak, 5 dips, air dried (not jet)	Unknown – visually very poor
SA005	0 – 10+	18 hour soak, 3 dips	very poor
SA006	0 – 12+	18 hour soak, 5 dips horizontally	poor

ELLIPSOMETRY

Used to investigate uniformity and thickness

Sample: **SA002**

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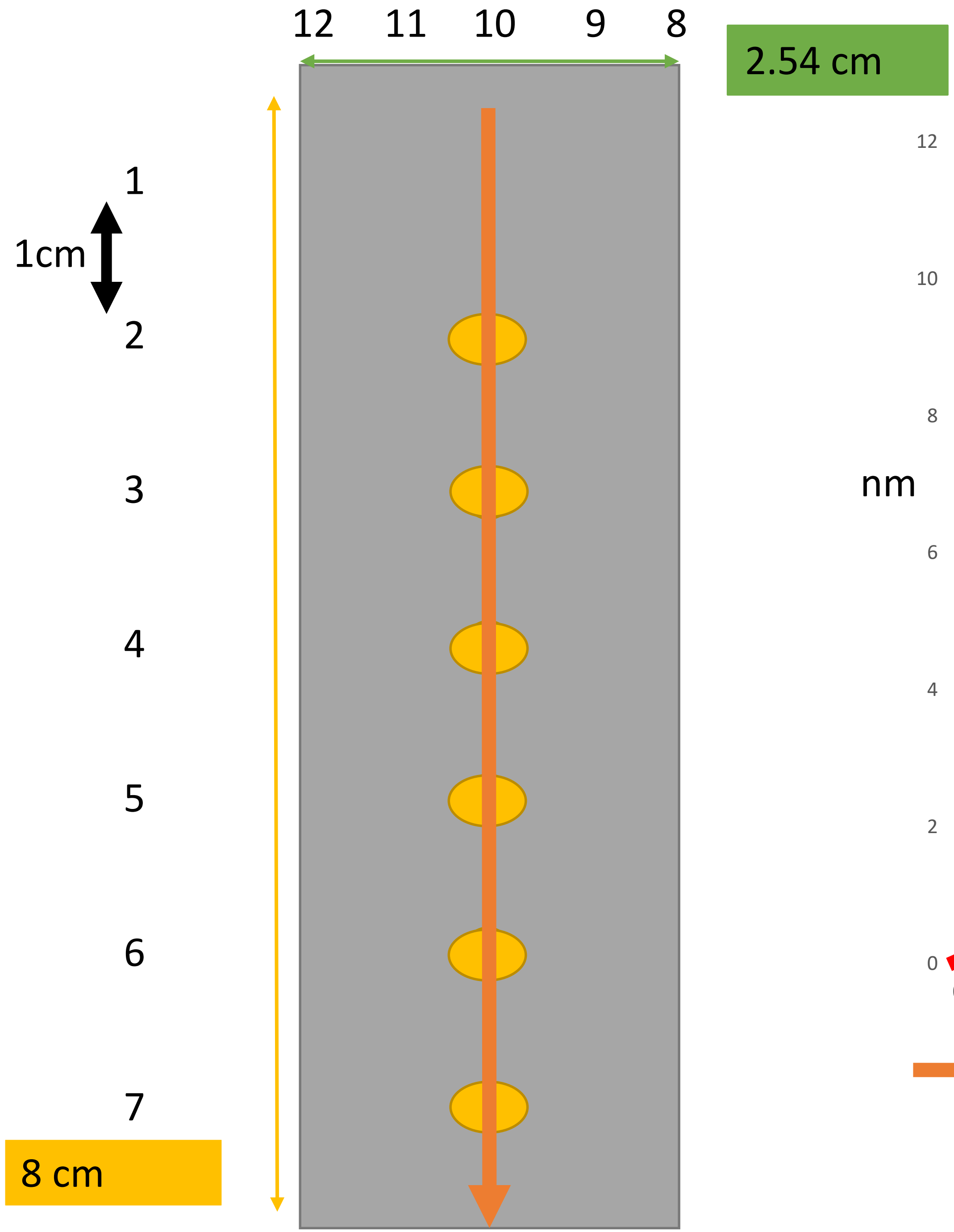
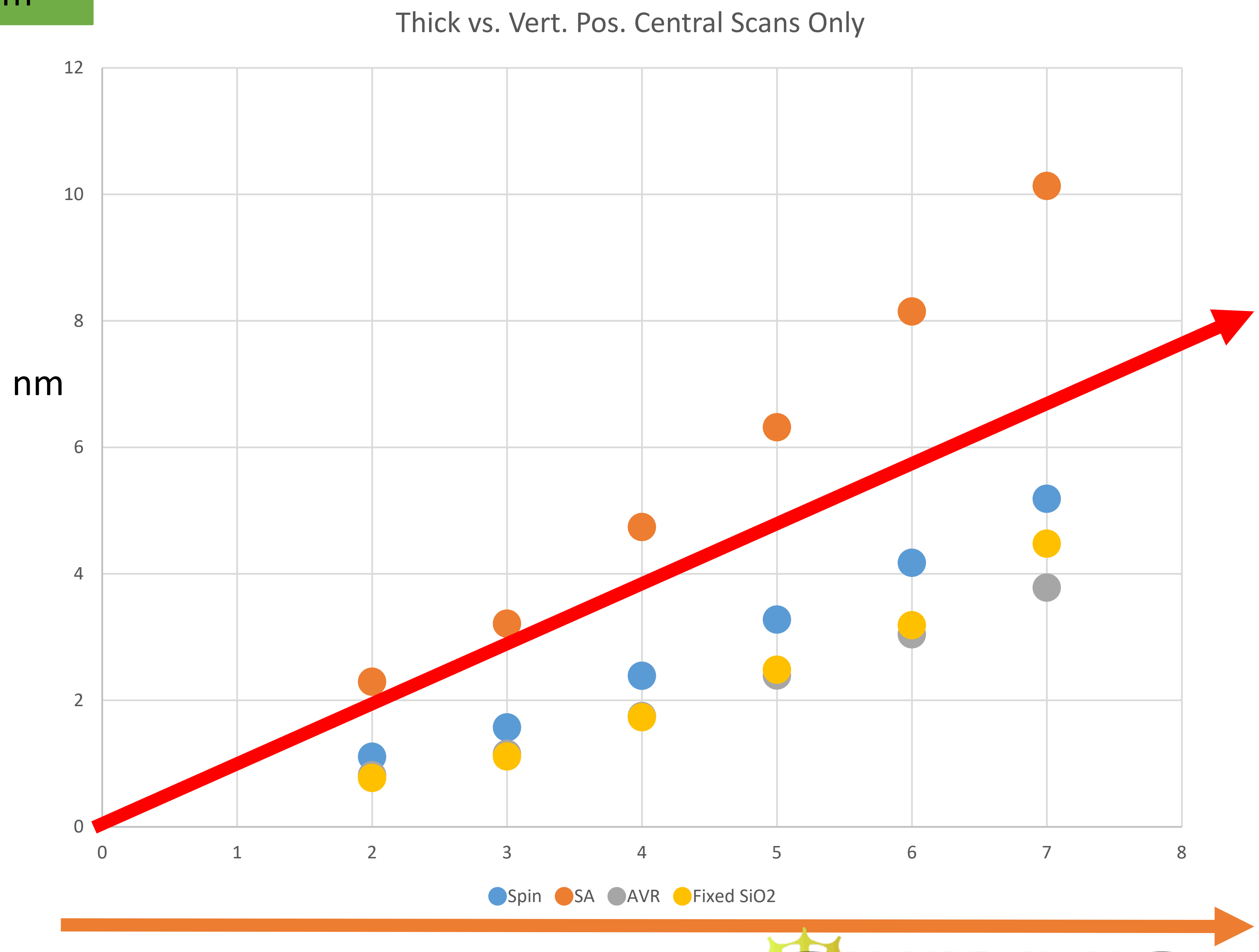
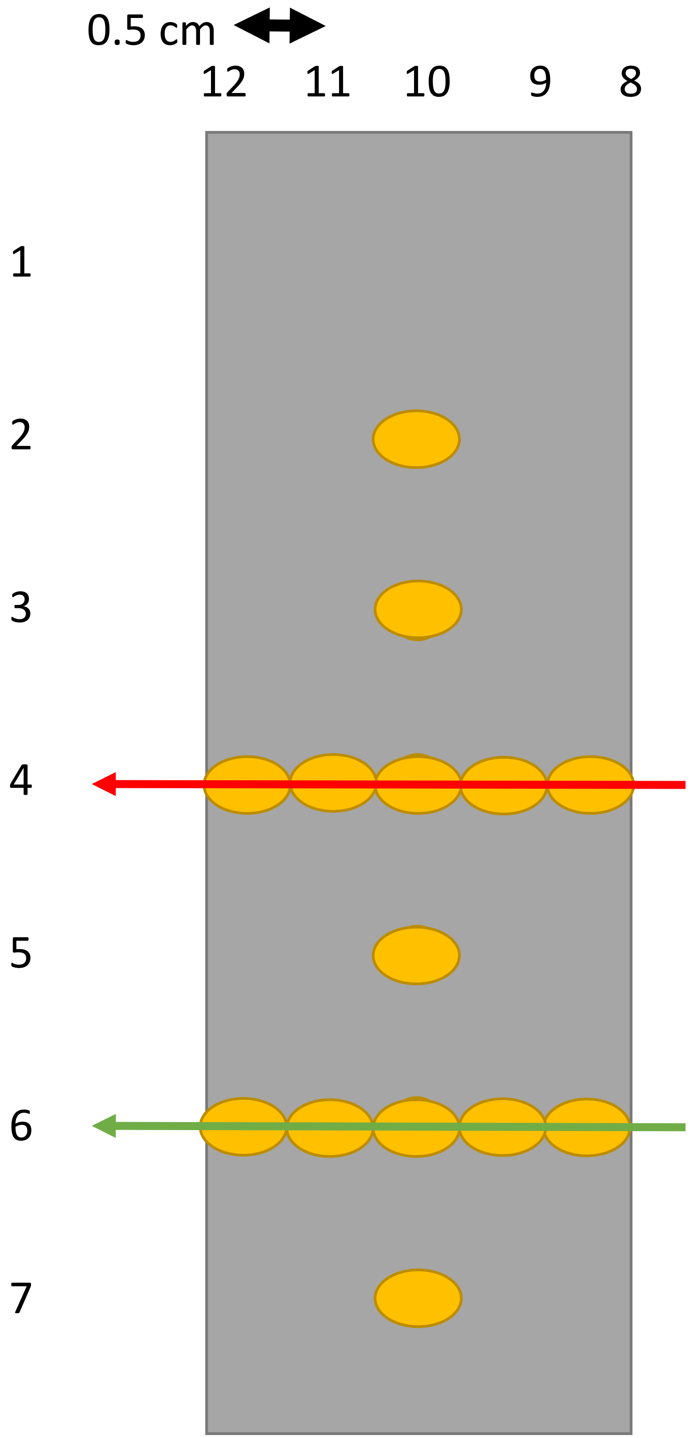
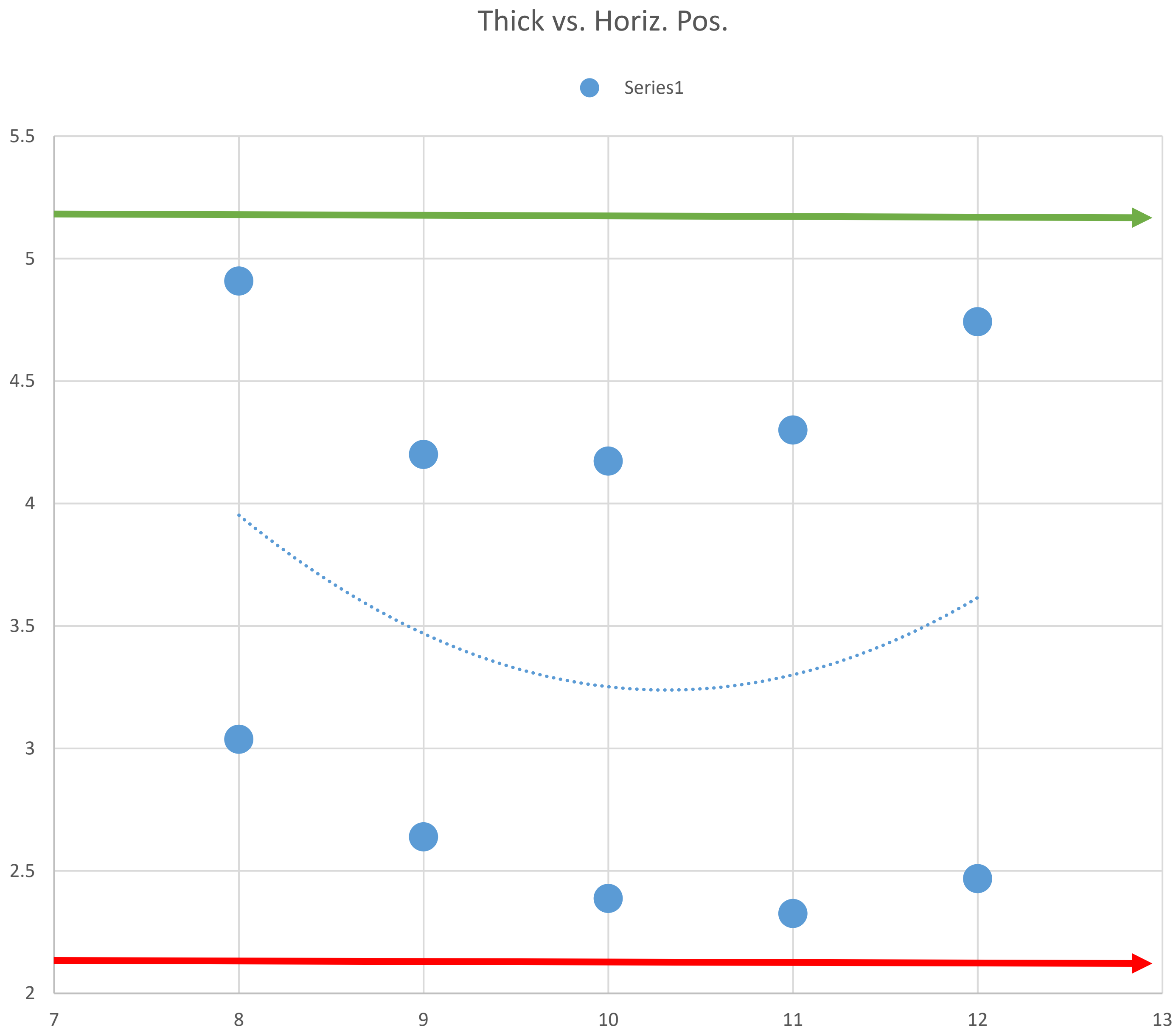


12
11
10
9
8
2.54 cm
1
1cm
2
3
4
5
6
7
8 cm

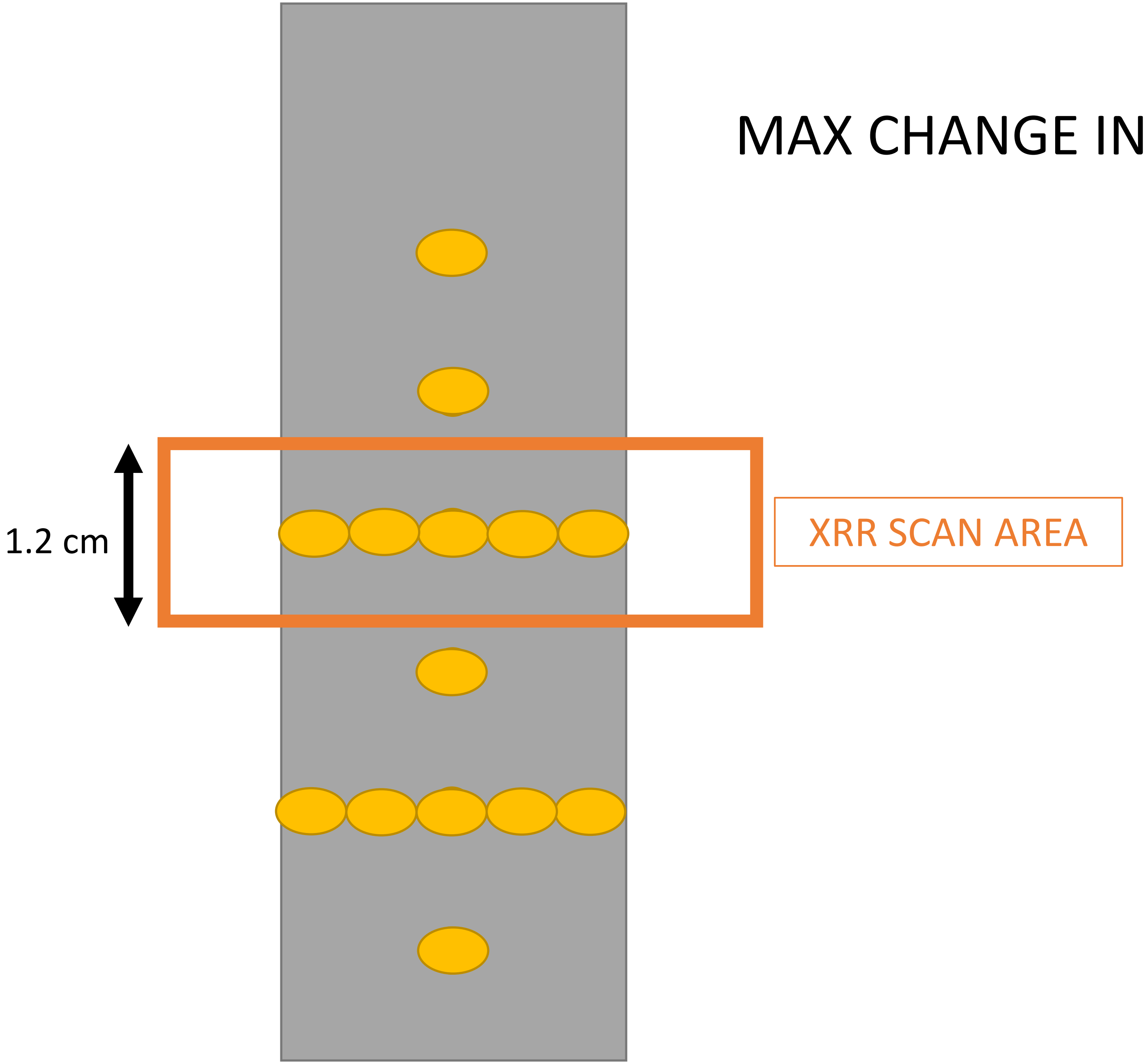


Thick vs. Vert. Pos. Central Scans Only
nm
0
2
4
6
8
10
12
0
1
2
3
4
5
6
7
8
Spin
SA
AVR
Fixed SiO2


0.5 cm
12
11
10
9
8
1
2
3
4
5
6
7


Thick vs. Horiz. Pos.
Series1
5.5
5
4.5
4
3.5
3
2.5
2
7
8
9
10
11
12
13

MAX CHANGE IN THICKNESS = about 2.3 nm



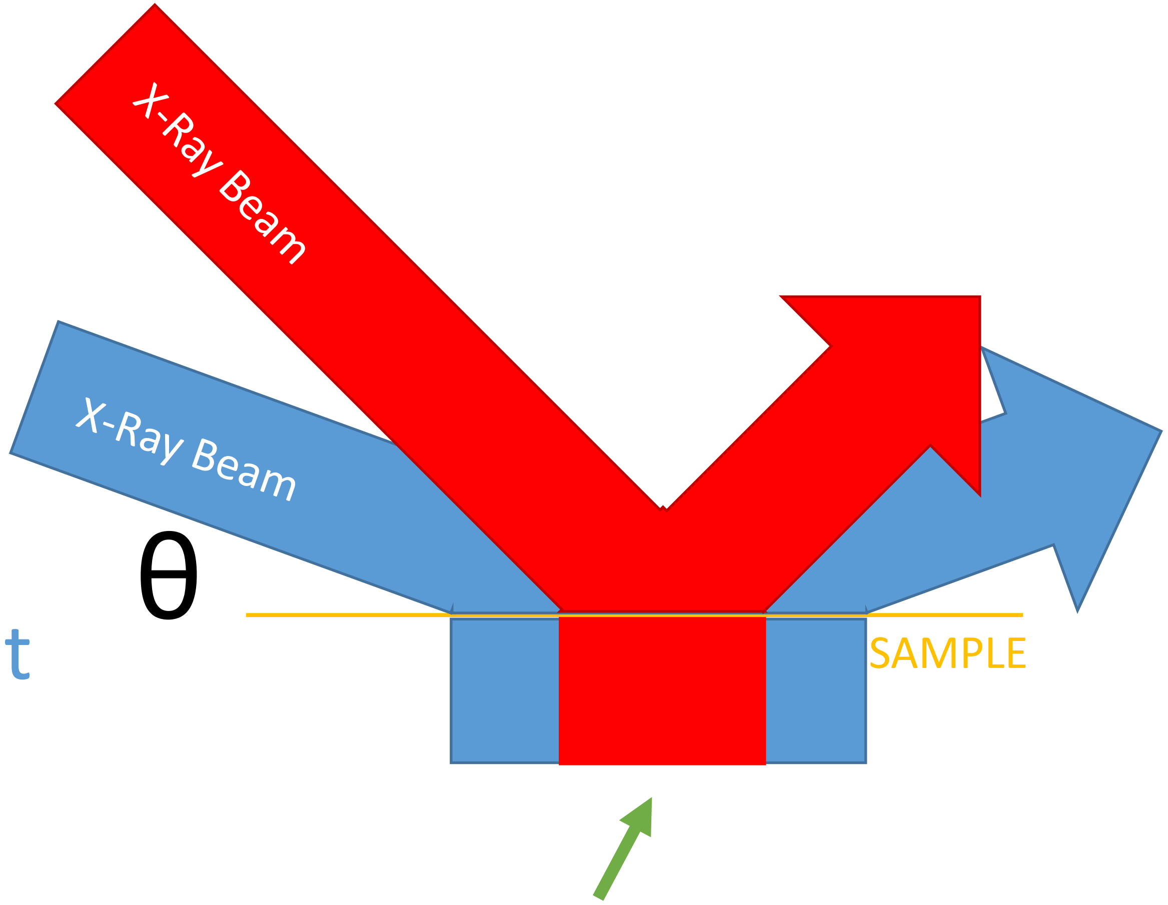
However, due to the angle changes in XRR…

Reflectometry Footprint

Higher Q = Higher source/detector angles

Higher angles = smaller area/footprint surveyed

Smaller Area = smaller non-uniformity

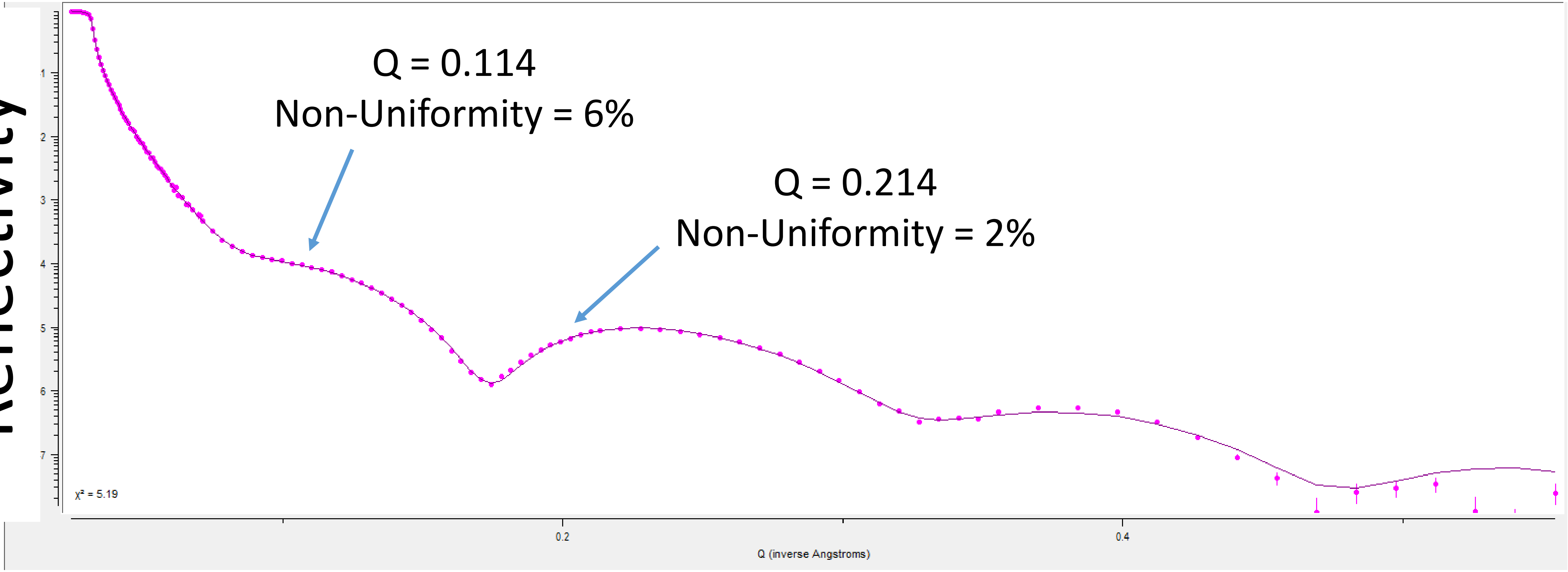


Footprint = (beam width)/sinθ

X-Ray Reflectometry Data

Anhydrous (<10% RH)

Reflectivity



0.5

Q (inverse Angstroms)

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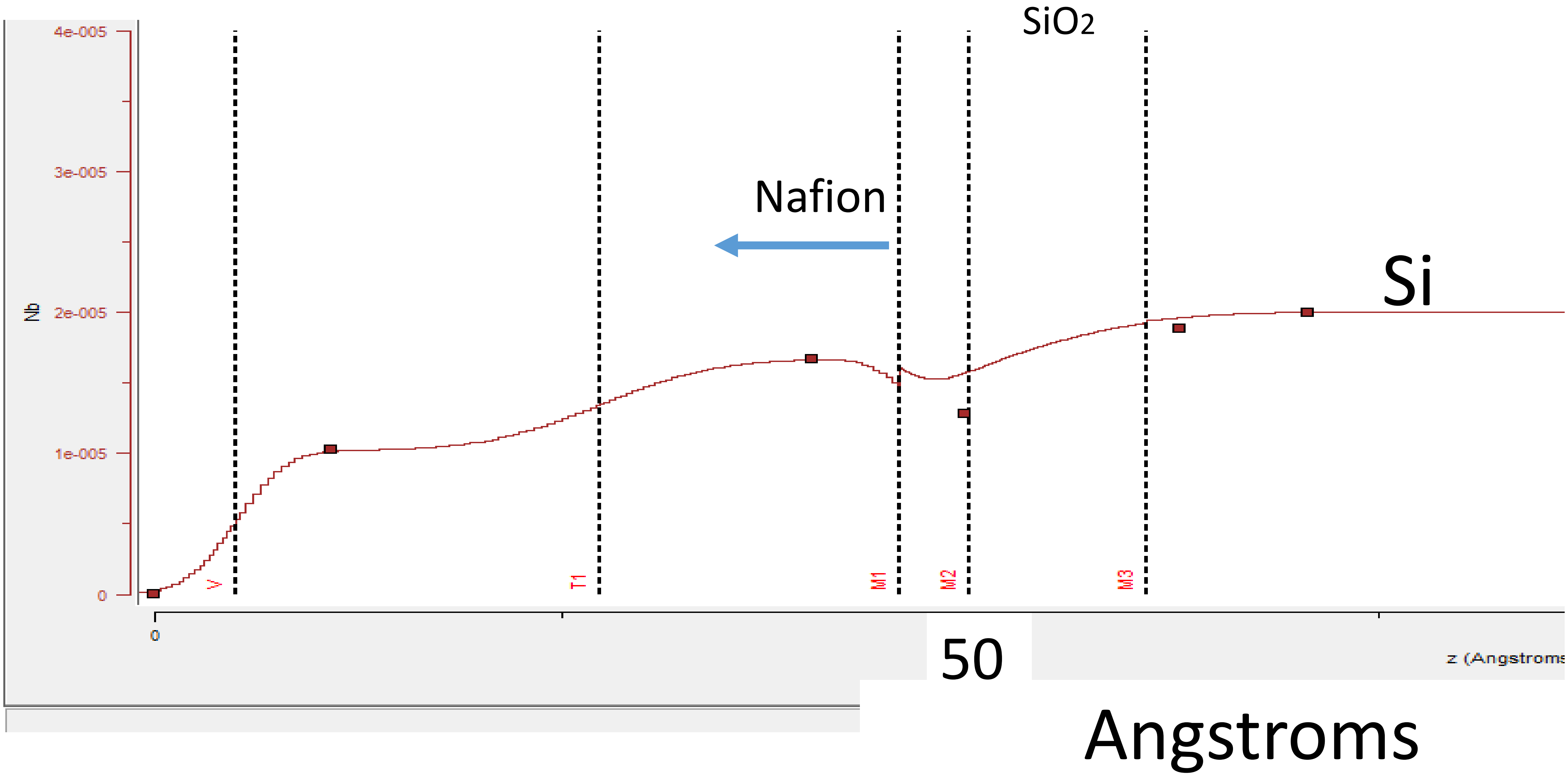
X-Ray Reflectometry Data Analysis

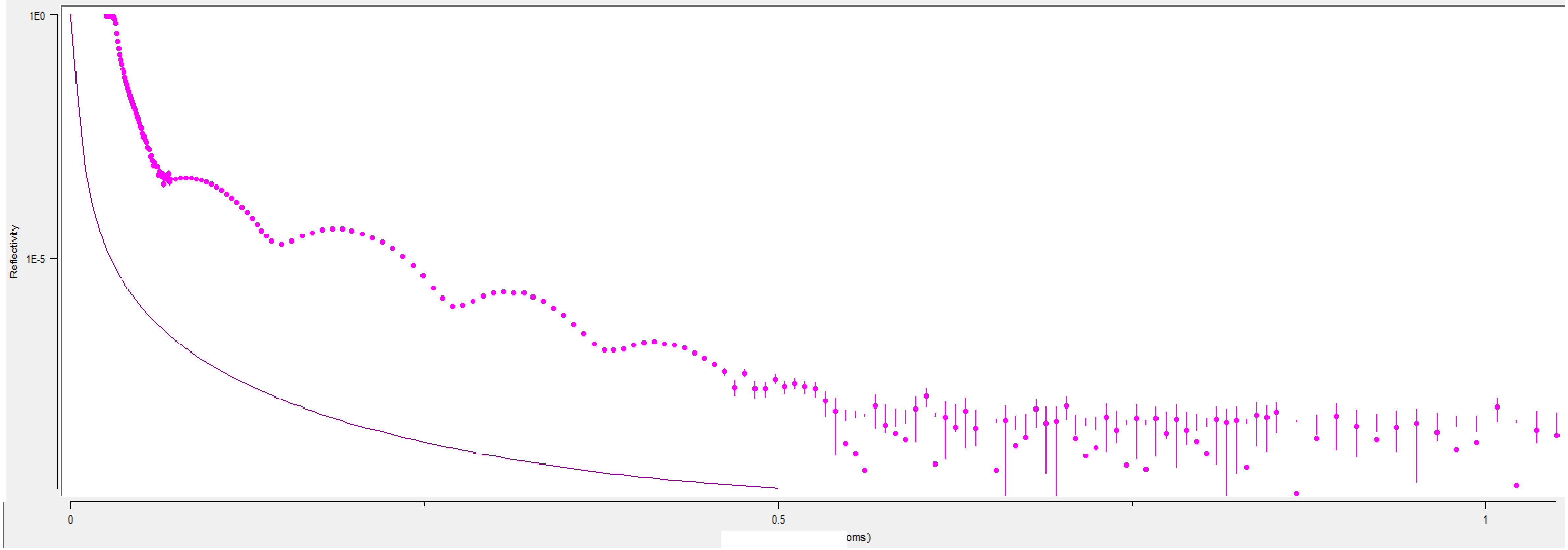


Unfit Data

Preliminary estimates of about 25% swelling volume

Hydrated (>90% RH)

Reflectivity



0.5

Q (inverse Angstroms)

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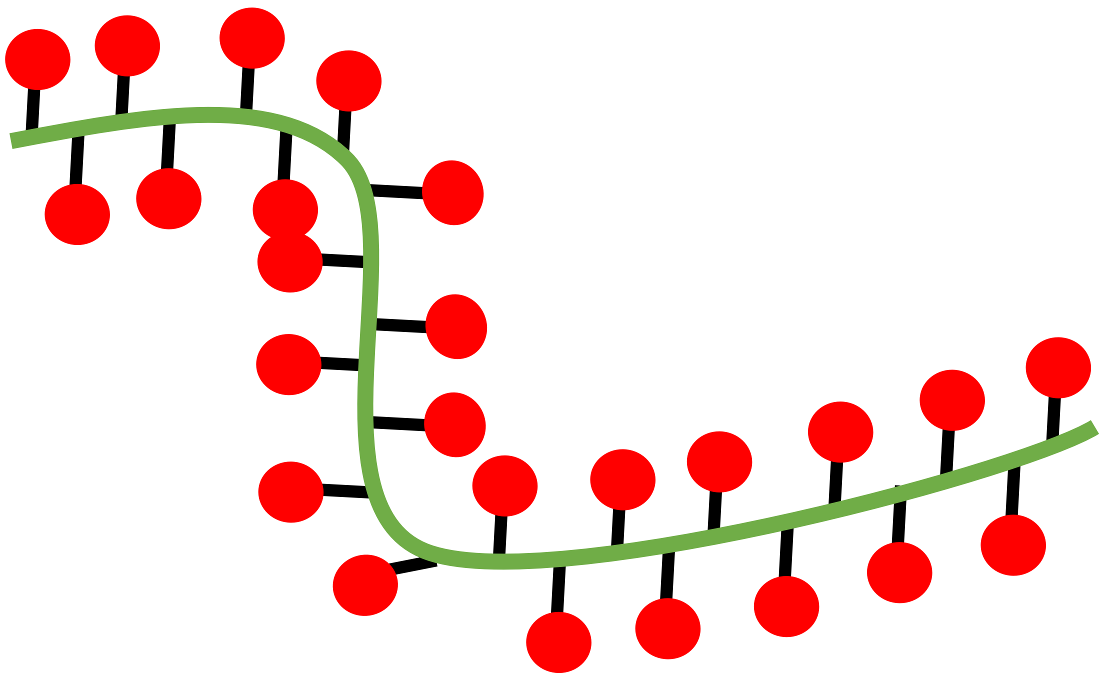
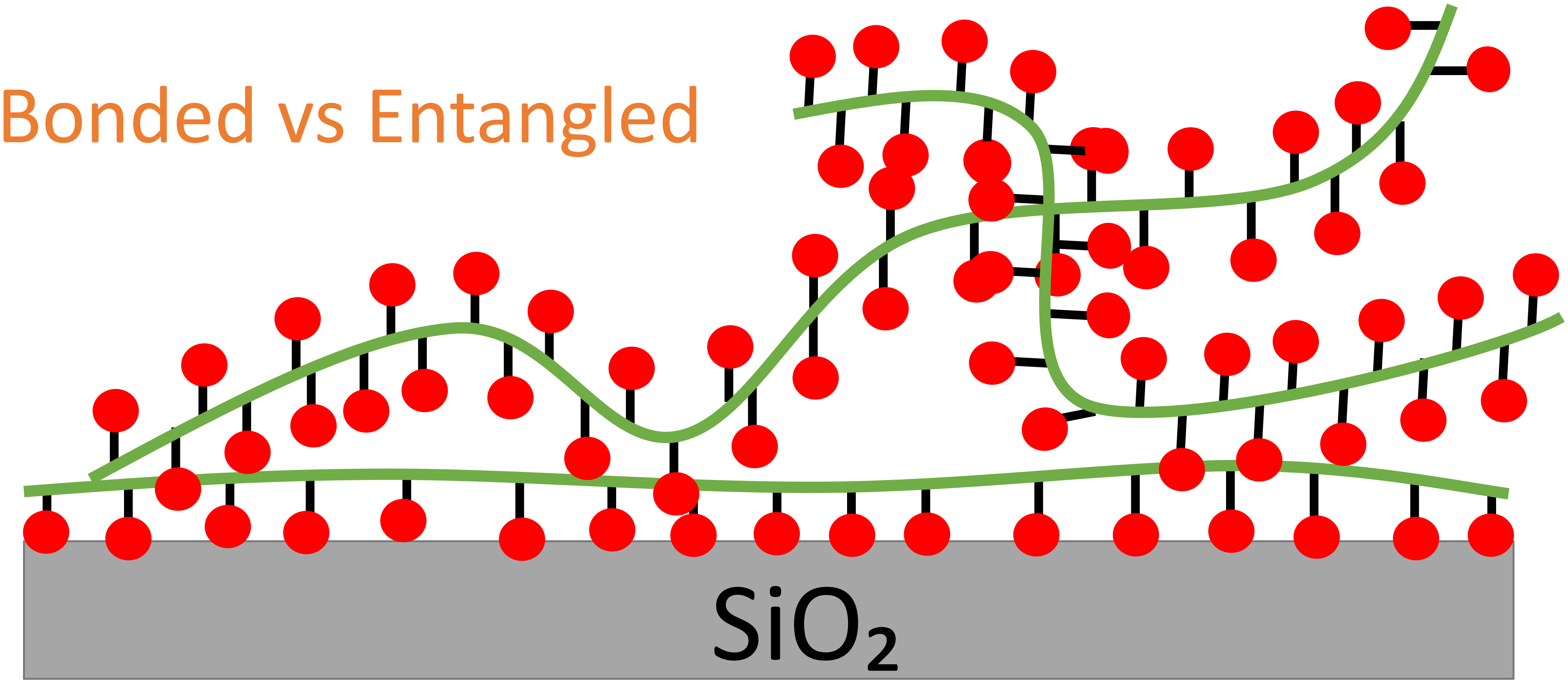


Proposed Physical Structural Model

- Bonded vs Entangled



Overall Conclusions

- Most deposited during drying, not during SA soak
- Because large fraction is deposited during drying step, uniformity is hard to achieve
- Goal Achieved: Create SA Ultrathin films suitable for XRR
- Goal Achieved: XRR shows structure in film corresponding to different parts of the molecule
- Goals to be pursued:
  - Films suitable for NR
  - Additional In situ QCM measurements for Nafion deposition with more sensitivity
  - Consistent and reproducible technique established for creating films
  - Investigate with Pt sputtered substrates

Acknowledgements

- NSF for support of SURF program
- Joe Dura – SURF mentor
- Steven Decaluwe – Colorado School of Mines Research Advisor
- Nhan Nguyen - Ellipsometer
- Andrew Vujcevic and Luke Waguespack – QCM tests done at CSM
- SURF Organizers

COLORADO SCHOOL OF MINES
EARTH ENERGY ENVIRONMENT

CHRNS CENTER FOR HIGH RESOLUTION NEUTRON SCATTERING NSF NIST

QUESTIONS?

Contact Info:

johfisch@mymail.mines.edu

BOOKMARK SLIDE 1

- EVERTHING BEFORE THIS IS NEARLY DONE

Citations

- Impact of Substrate and Processing on Confinement of Nafion Thin Films A. Kusoglu, D. Kushner, D. K. Paul, K. Karan, M. A. Hickner, and A. Z. Weber *Adv. Funct. Mater.* **24**, pp. 4763-4774 2014
- Atomic Force Microscopy Studies on the Dewetting of Perfluorinated Ionomer Thin Films T. A. Hill, D. L. Carroll, R. Czerw, C. W. Martin, and D. Perahia *Journal of Polymer Science: Part B: Polymer Physics* **41** pp. 149-158 2003
- Characteristics of Self-Assembled Ultrathin Nafion Films D. K. Paul, K. Karan, A. Docoslis, J. B. Giorgi, and J. Pearce *Macromolecules* **46** pp. 3461-3475 2013
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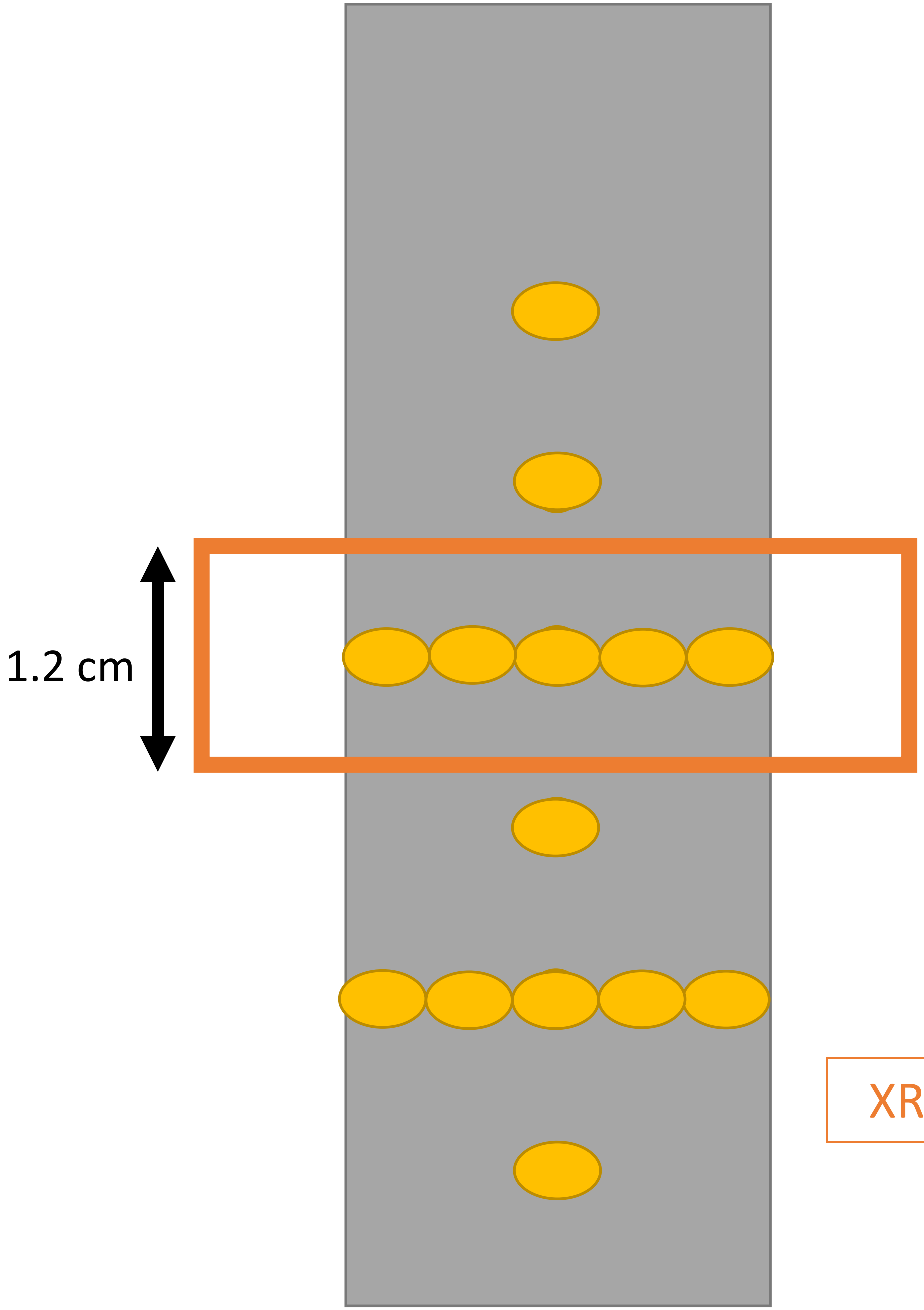
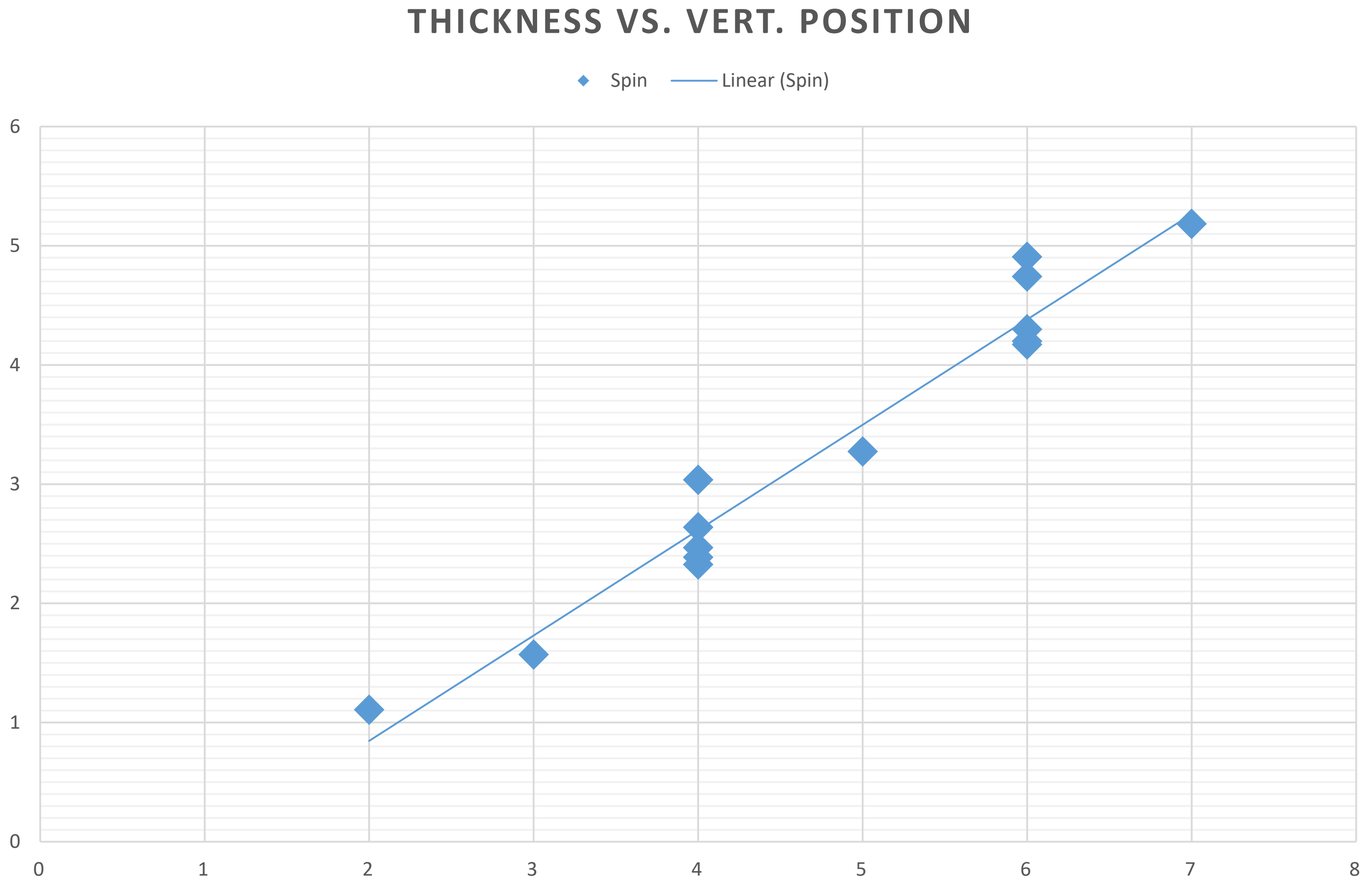
FITTING SOFTWARE USED

- J.R. Woollam for Ellipsometry data fitting software
- Refl1d/Reflpak for Reflectivity data fitting

INTERNET SOURCED IMAGES

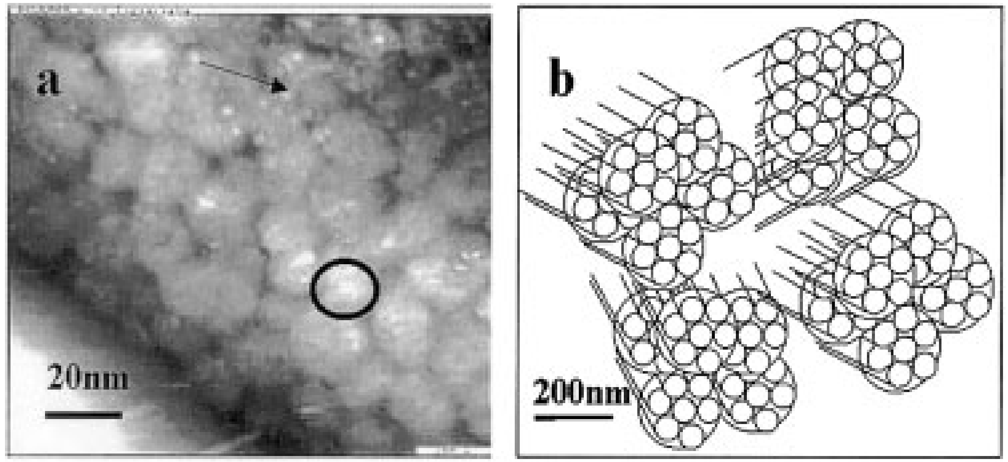
- http://www.doitpoms.ac.uk/tlplib/fuel-cells/pem_membrane.php
- "Ellipsometry setup" by en: User: Buntgarn, traced by User:Stannered - en:Image:Ellipsometry setup.jpg. Licensed under CC BY-SA 3.0 via Wikimedia Commons - https://commons.wikimedia.org/wiki/File:Ellipsometry_setup.svg#/media/File:Ellipsometry_setup.svg
- http://physics.valpo.edu/staff/arichter/XRR.htm





MAX CHANGE IN THICKNESS = about 2.3 nm

Hill et al.



- "Shear force drives polymer away from thermodynamic equilibrium, and due to intermolecular forces this may not be solved through annealing as typical"
- "The aggregation poses a challenge for forming a molecularly thin, homogeneous film"
- No shear force induced, yet overall more difficult to produce

Atomic Force Microscopy Studies on the Dewetting of Perfluorinated Ionomer Thin Films T. A. Hill, D. L. Carroll, R. Czerw, C. W. Martin, and D. Perahia *Journal of Polymer Science: Part B: Polymer Physics* **41** pp. 149-158 2003

Parallel line cuts from GISAXS intensity profiles

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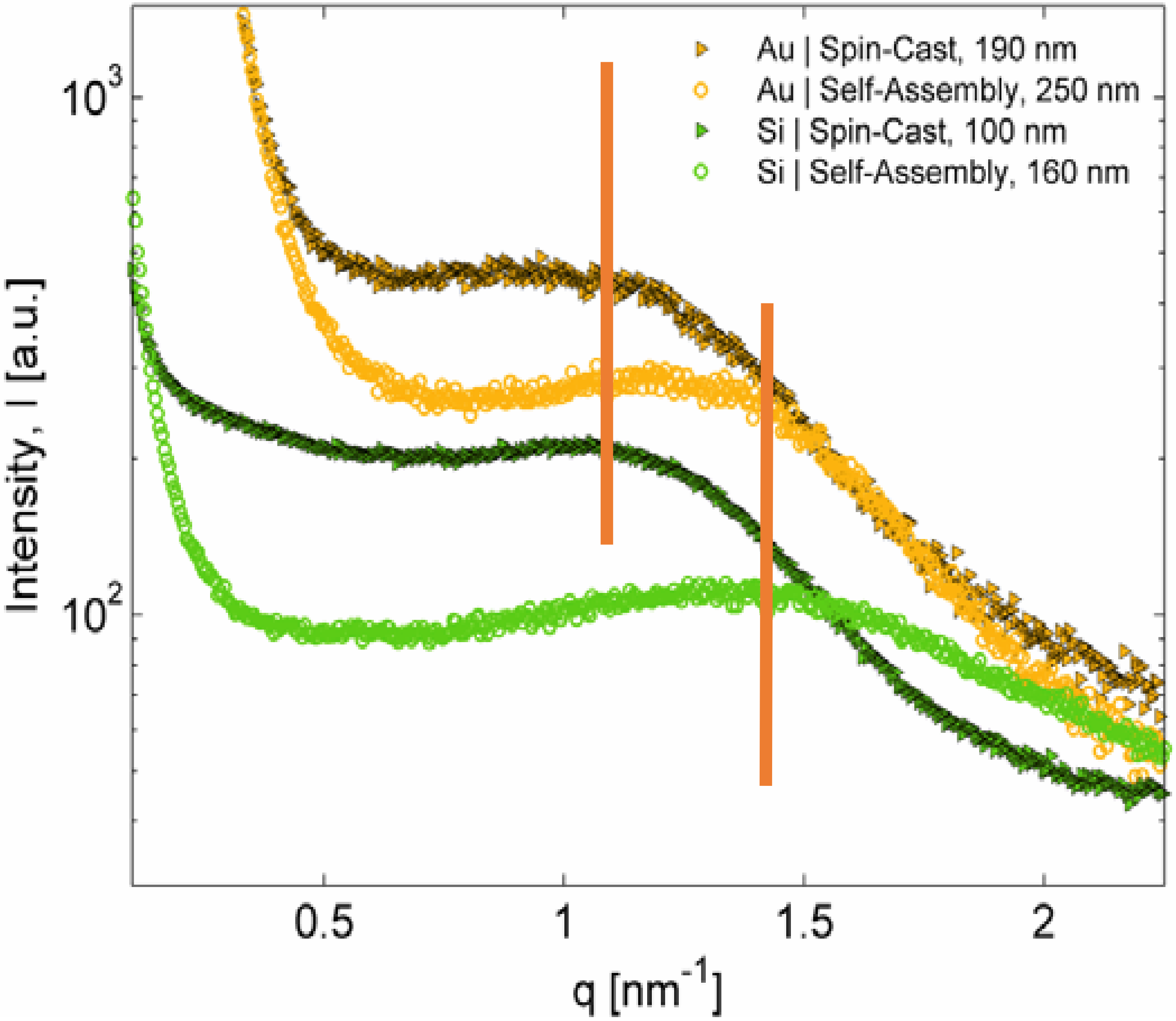
Noticeable differences between Self-Assembled and Spin-Cast both before and after annealing



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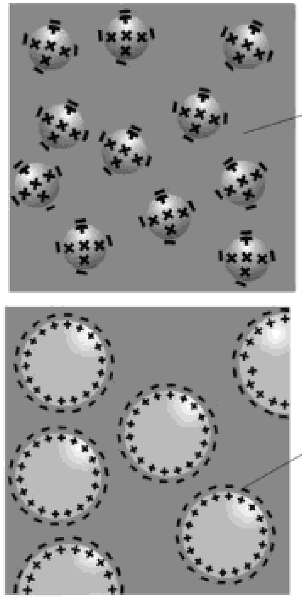
Increasing Water Fraction

Too little = no conduction

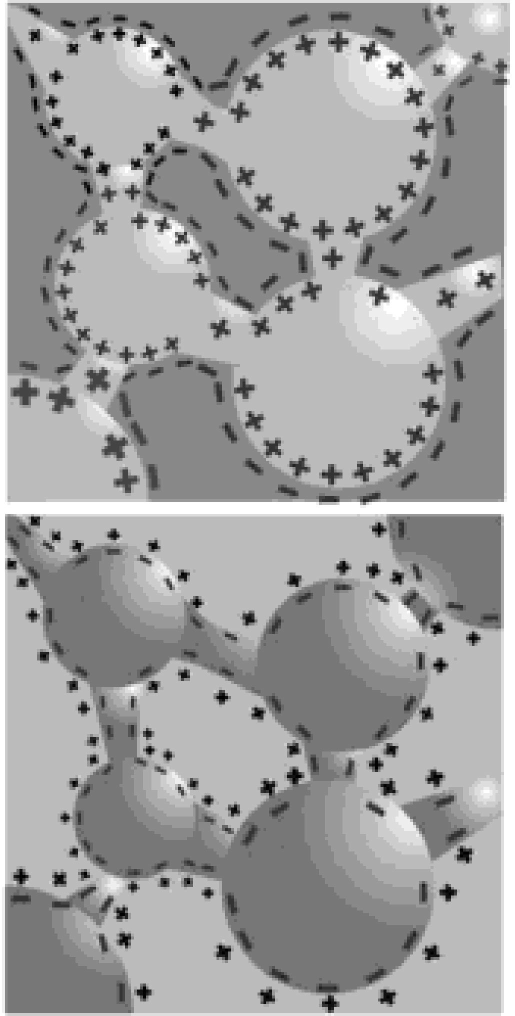


DRY MEMBRANE

Perfluorinated matrix

SWOLLEN MEMBRANE

Ionic domains



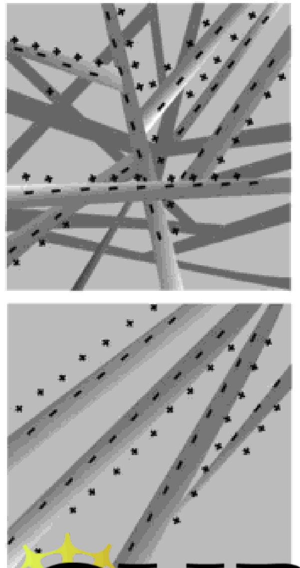
PERCOLATION

"STRUCTURE INVERSION"

Too much = no conduction

Water floods electrodes blocking O and H flow

Structural Integrity Lost

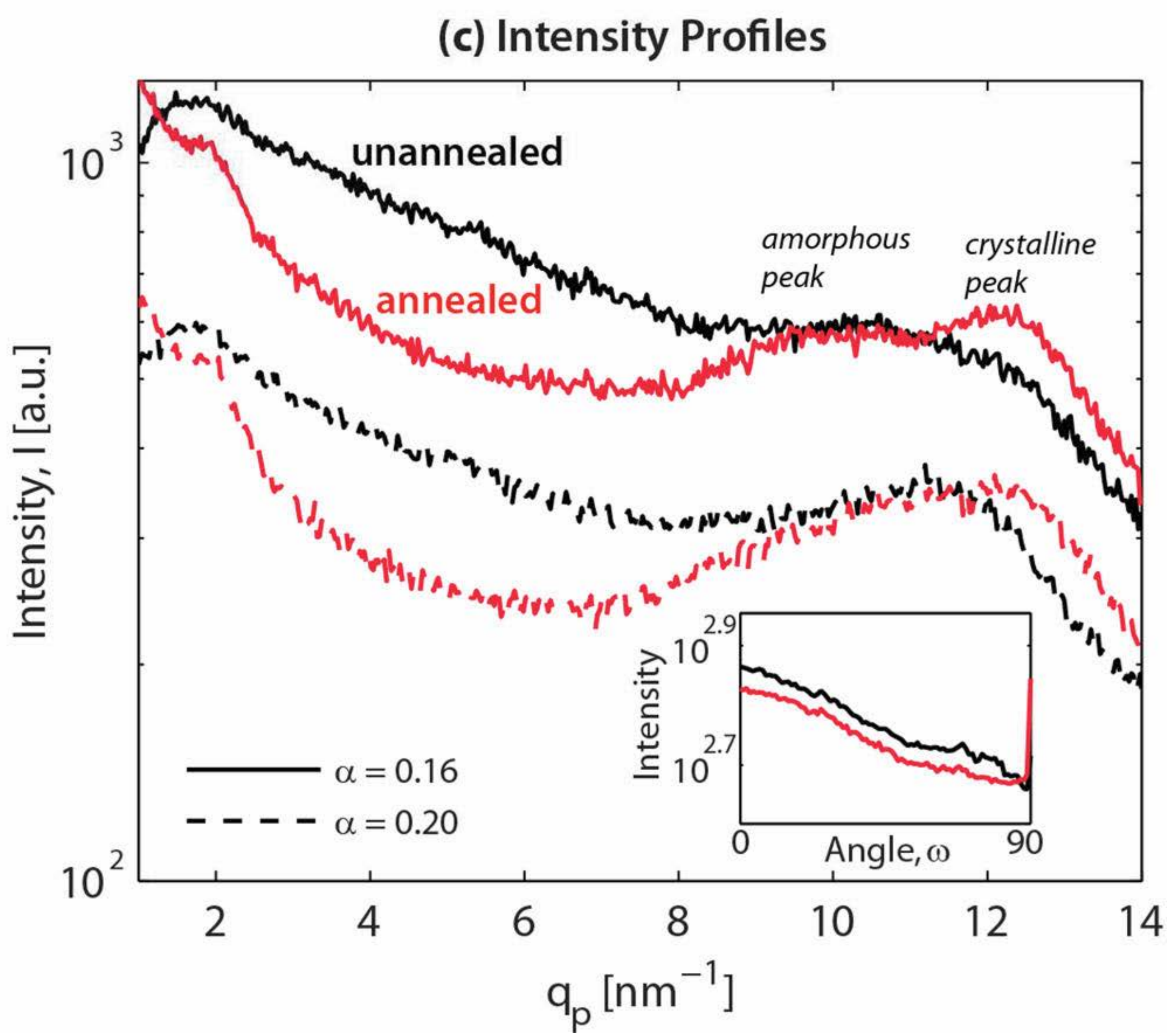


CONNECTED NETWORK OF POLYMERS RODS

COLLOIDAL DISPERSION OF ROD LIKE PARTICLES

State of Understanding of Nafion K. A. Mauritz and R. B. Moore *Chemical Reviews* **104** pp. 4535-4585 2004

Bulk Nafion Structure



Impact of substrate and processing

LITERATURE VALUES

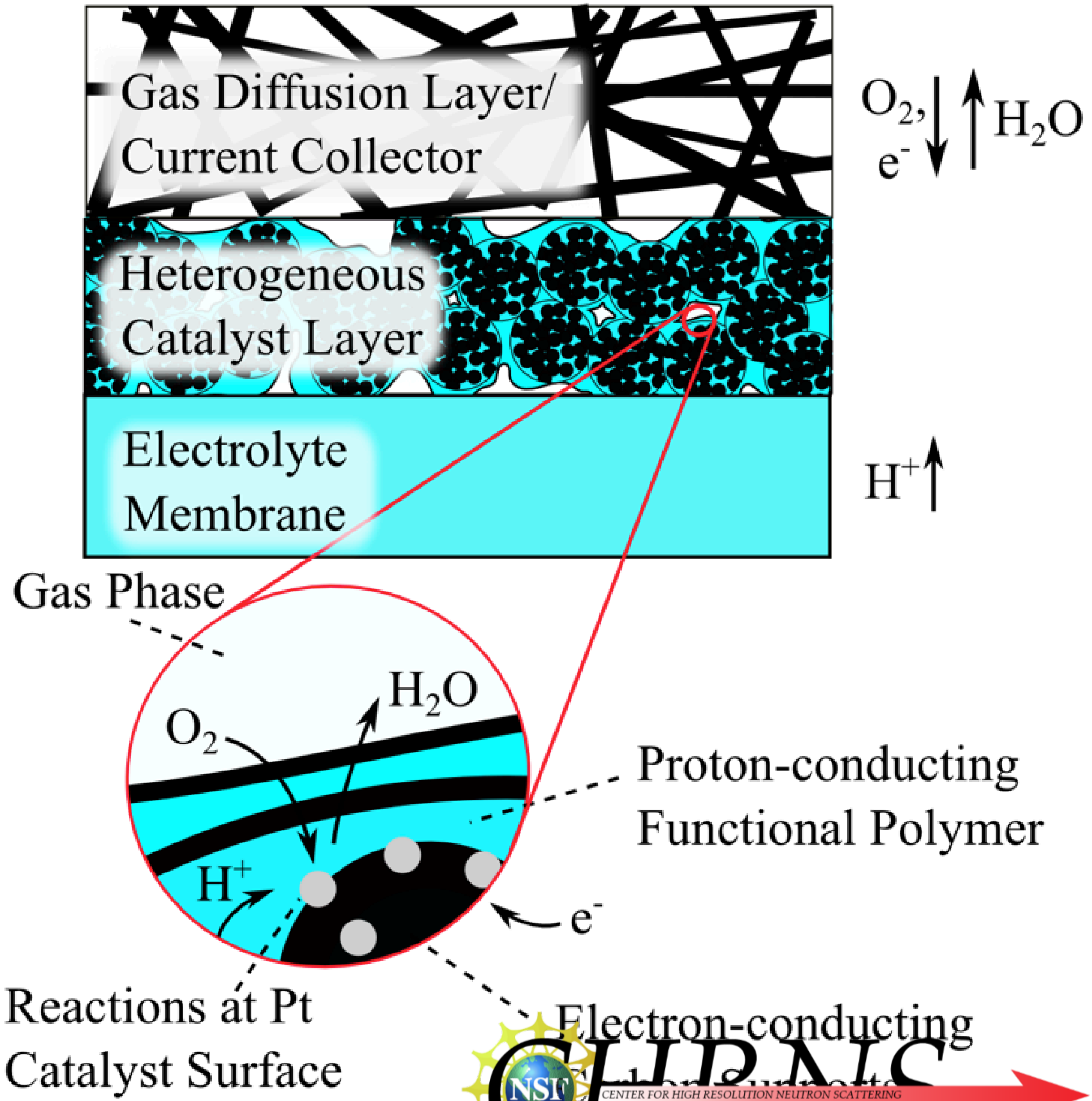
Reported for spin coated:

A = 1.353 B = -0.0018

Reported for SA:

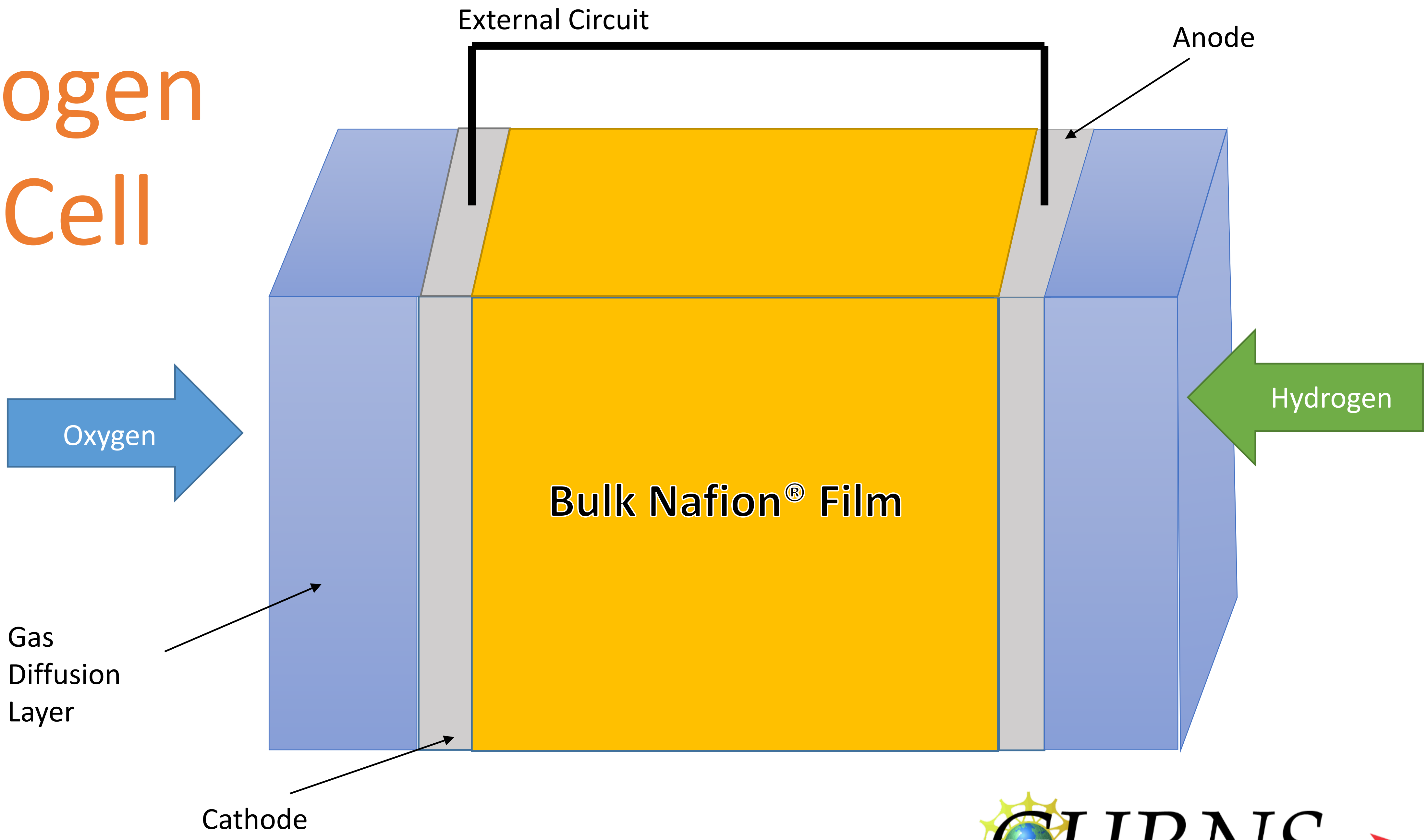
Nafion conc. (wt %)	Cauchy Coefficients A	B	C	Thickness (nm)	*n* (5500 Å)	Non-uniformity (%)
0.1	1.186	-0.0065	0	3.8±0.43	1.16	2.96
0.25	1.294	0.0021	0	10.5±0.22	1.30	4.41
0.5	1.385	-0.0049	0	31.4±0.46	1.37	9.86
1.0	1.388	-0.0052	0	57.1±0.95	1.37	17.07
3.0	1.358	0.0034	0	160.1±0.85	1.37	8.81
5.0	1.382	0.0031	0	307.7±6.07	1.39	24.25

PEMFC



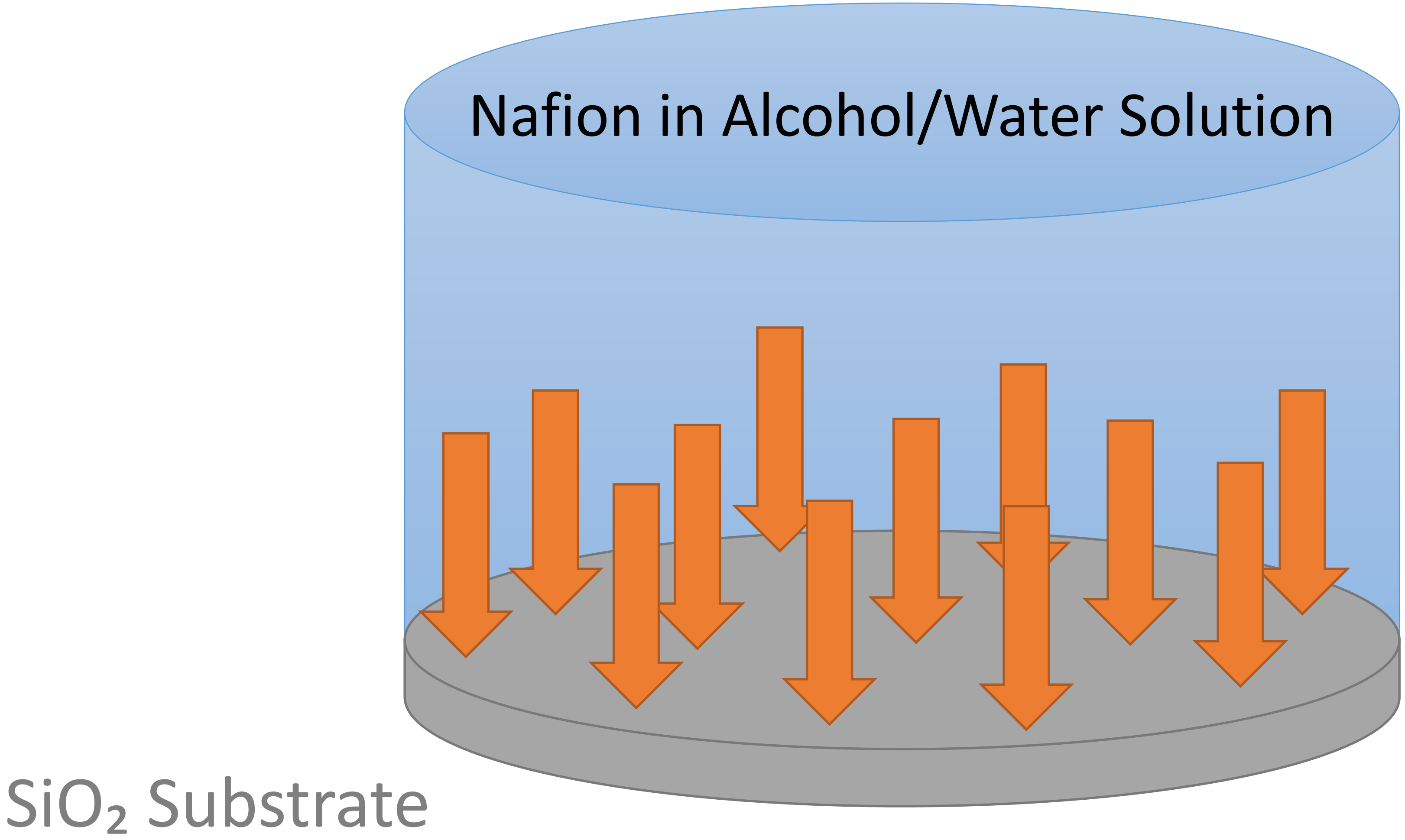
Gas Diffusion Layer/
Current Collector
O_2, e^-
H_2O
Heterogeneous
Catalyst Layer
Electrolyte
Membrane
H^+
Gas Phase
O_2
H_2O
H^+
e^-
Proton-conducting
Functional Polymer
Reactions at Pt
Catalyst Surface
Electron-conducting

Hydrogen Fuel Cell



Self-Assembly

No forces induced during deposition process



Nafion® molecules will spontaneously deposit on the substrate over time

BOOKMARK SLIDE 2

- EVERTHING AFTER THIS IS FAR FROM DONE But before here is in production or done (at least in order)

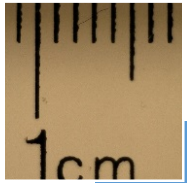
Procedure Description (Literature)

- The cleaned substrate was immersed in the Nafion solution of known concentration contained in a capped beaker.
- The substrate was exposed to Nafion solutions for 12 h or otherwise specified time.
- After carefully removing the substrate from the solution it was dried under a flow of dry air.
- The samples were subjected to a washing step soon after withdrawal of the substrate from the Nafion solution to ensure that any adhering liquid and weakly held Nafion molecules were removed.
- The washing step consisted of instantaneously dipping the solution exposed substrate into a beaker containing the same solvent that made up the Nafion solution.
- The washed substrate was then dried in a stream of compressed air.

Characteristics of Self-Assembled Ultrathin Nafion Films
Devproshad K. Paul,† Kunal Karan,†,‡,* Aristides Docoslis,† Javier B. Giorgi,§ and Joshua Pearce⊥,∥

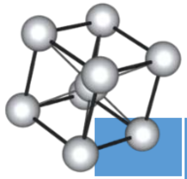
NR interface structure sensitivity (summary of overall goal)

Significance



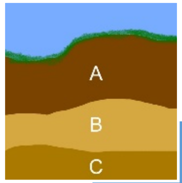
Standardization

- Standardization for future experimentation
- Give a more concrete definition of “Self-Assembly” for Nafion® films



Structure

- Establish structural characteristics of Self-Assembled Nafion® ultra-thin films
- Try to explain characteristics through structure



Binding Properties

- Substrate and Nafion® Bonding properties
- Nafion® Molecule Orientation and layering
- Explain macromolecular structure through intermolecular forces

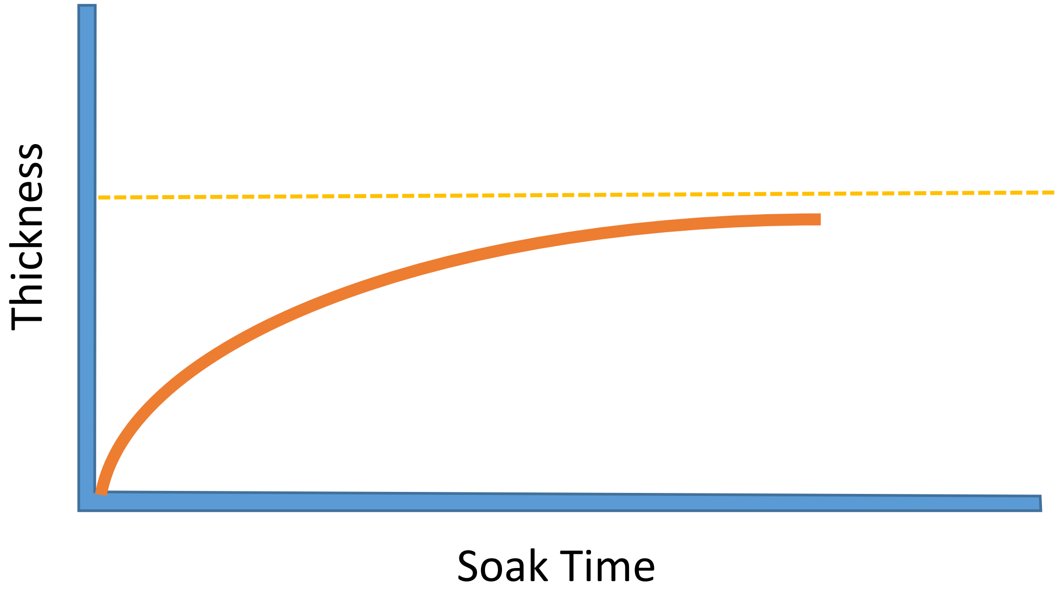
ANALYSIS

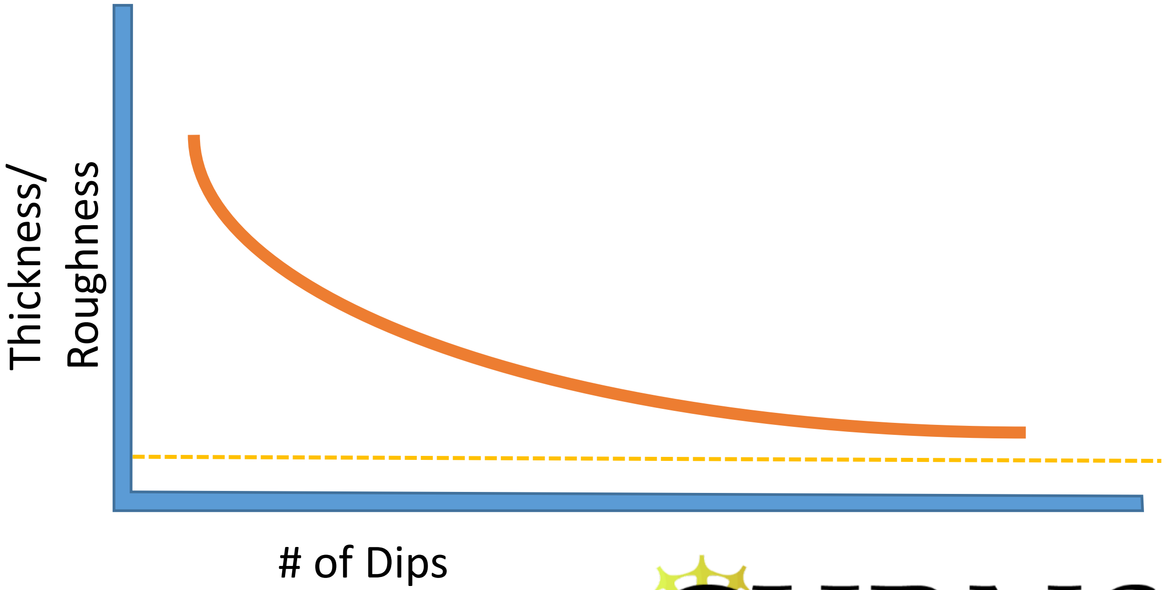
PRELIMINARY CONCLUSIONS or THOUGHTS


NO ENTRY
BEAM ON
BEAM OFF
MAGIK LOCAL SHUTTER
CHRNS
CENTER FOR HIGH RESOLUTION NEUTRON SCATTERING

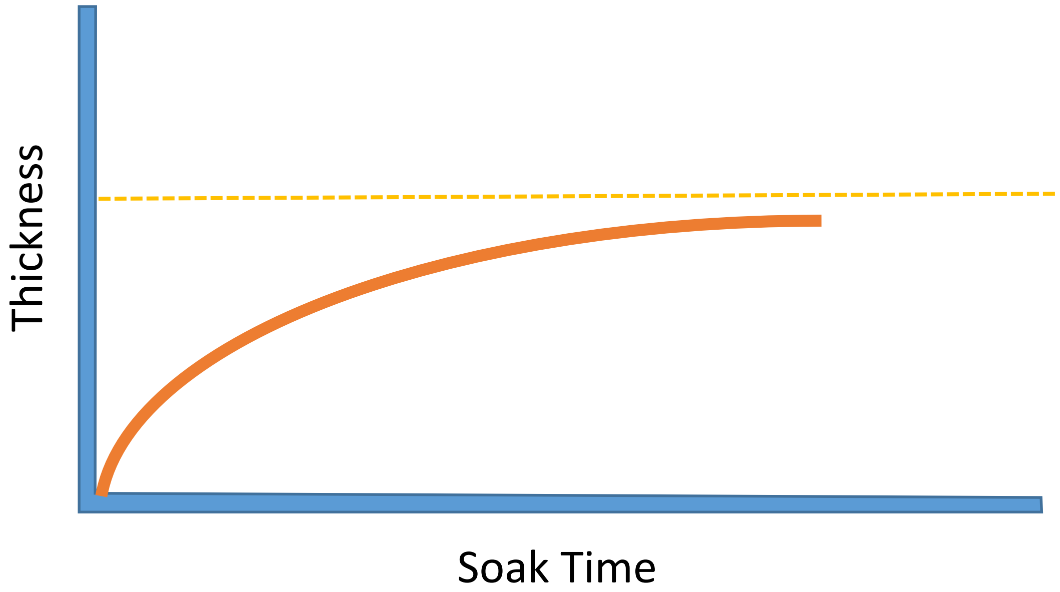
Nafion® Self-Assembly Models

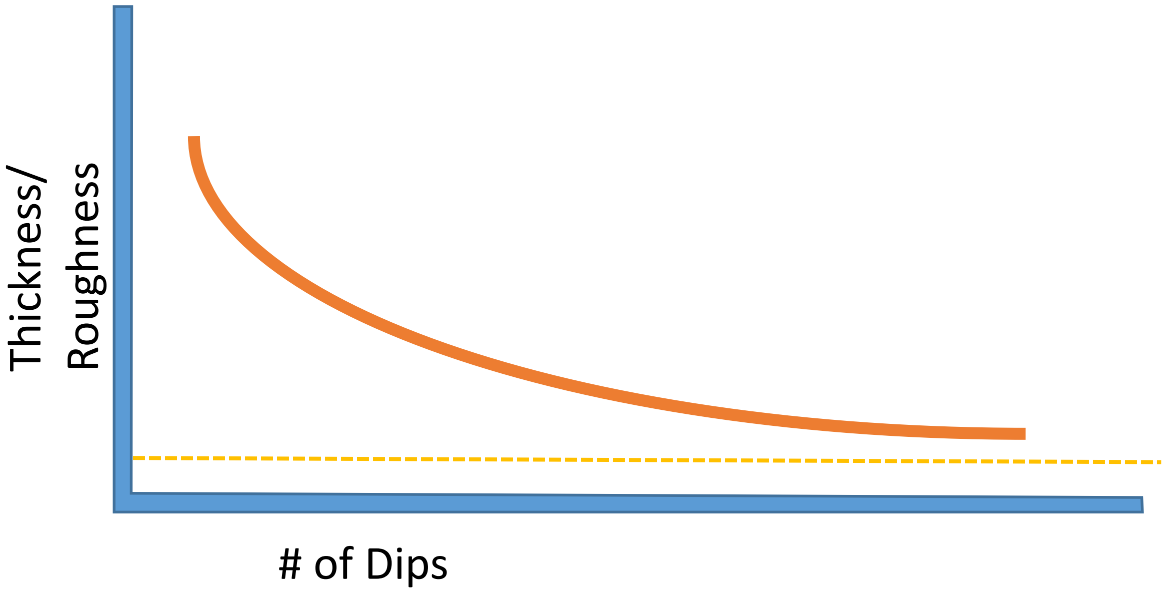
- Soak time vs. Thickness
- Dips vs. Thickness/Roughness (should look relatively similar)
- Predicted Results:



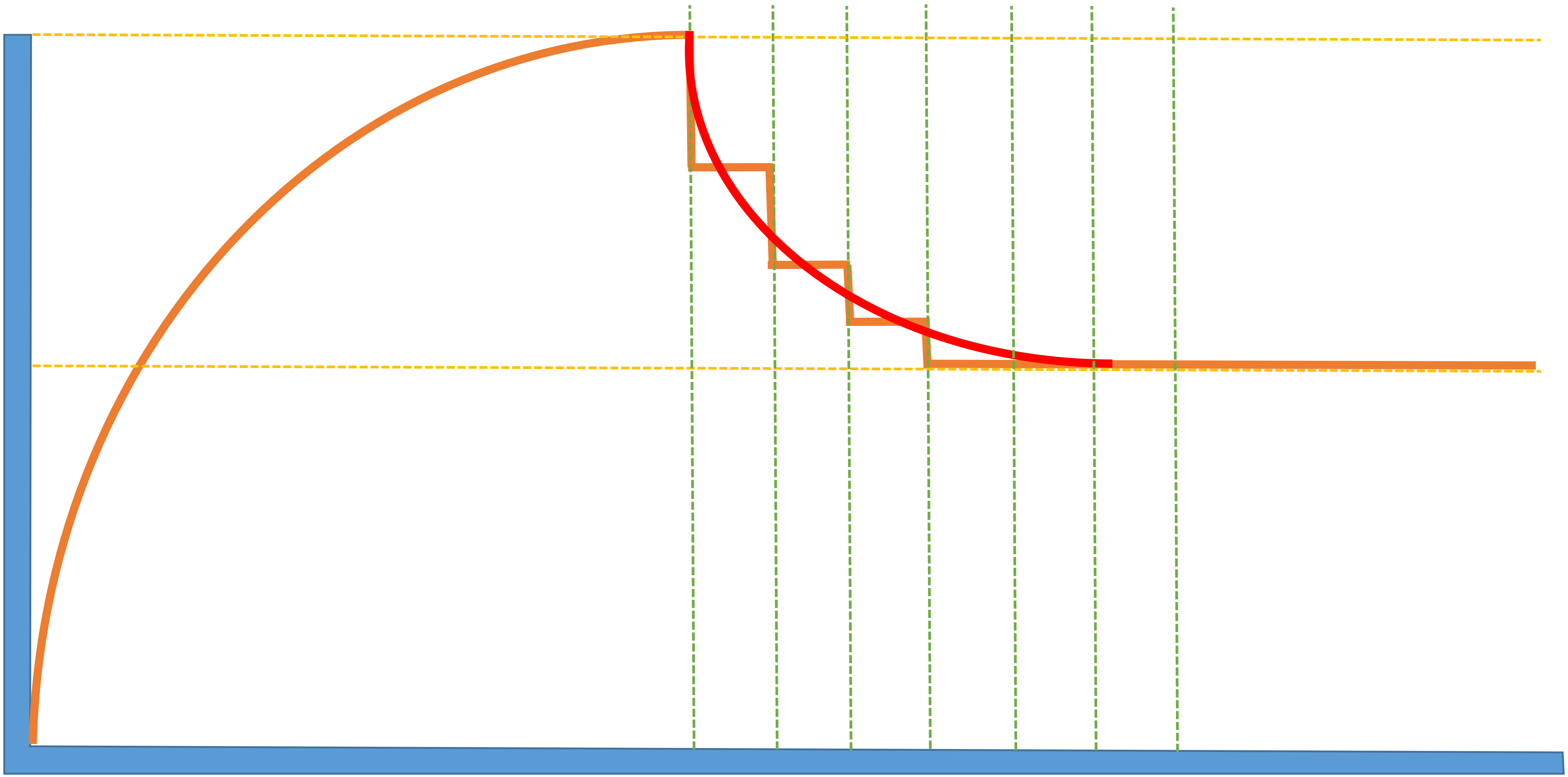


CHRNS CENTER FOR HIGH RESOLUTION NEUTRON SCATTERING NSF NIST

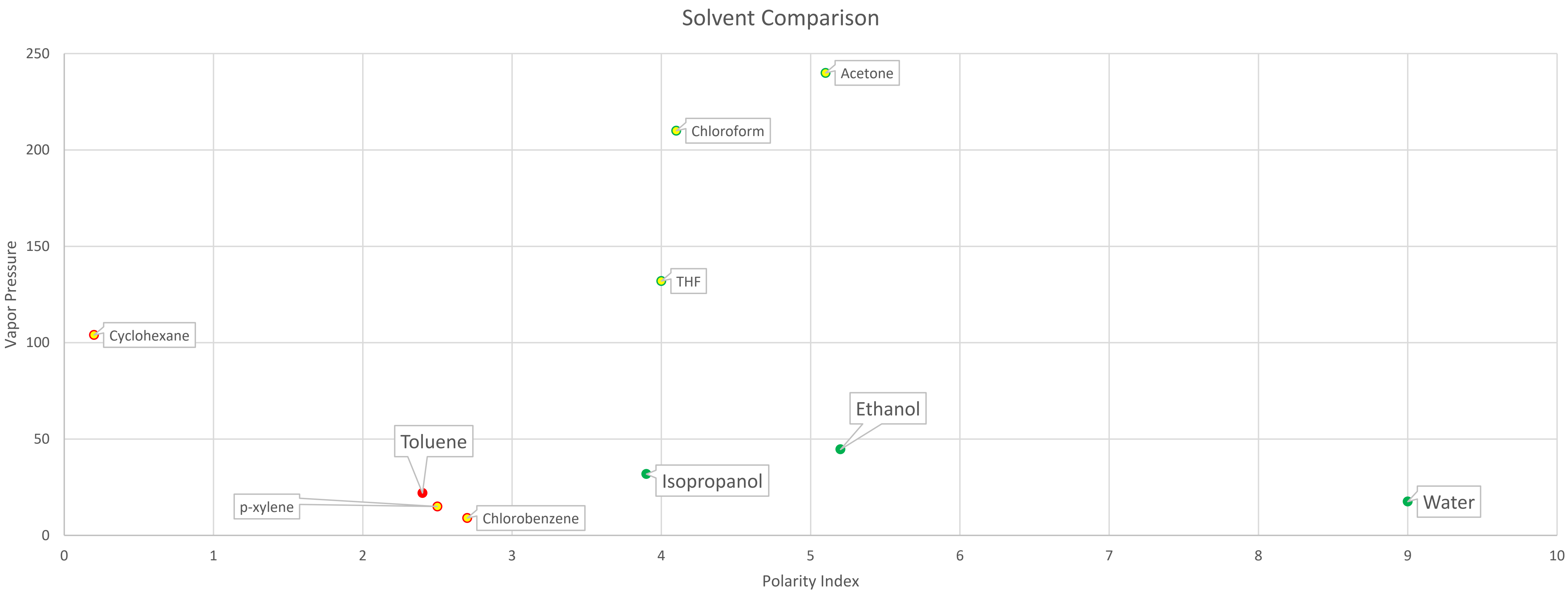




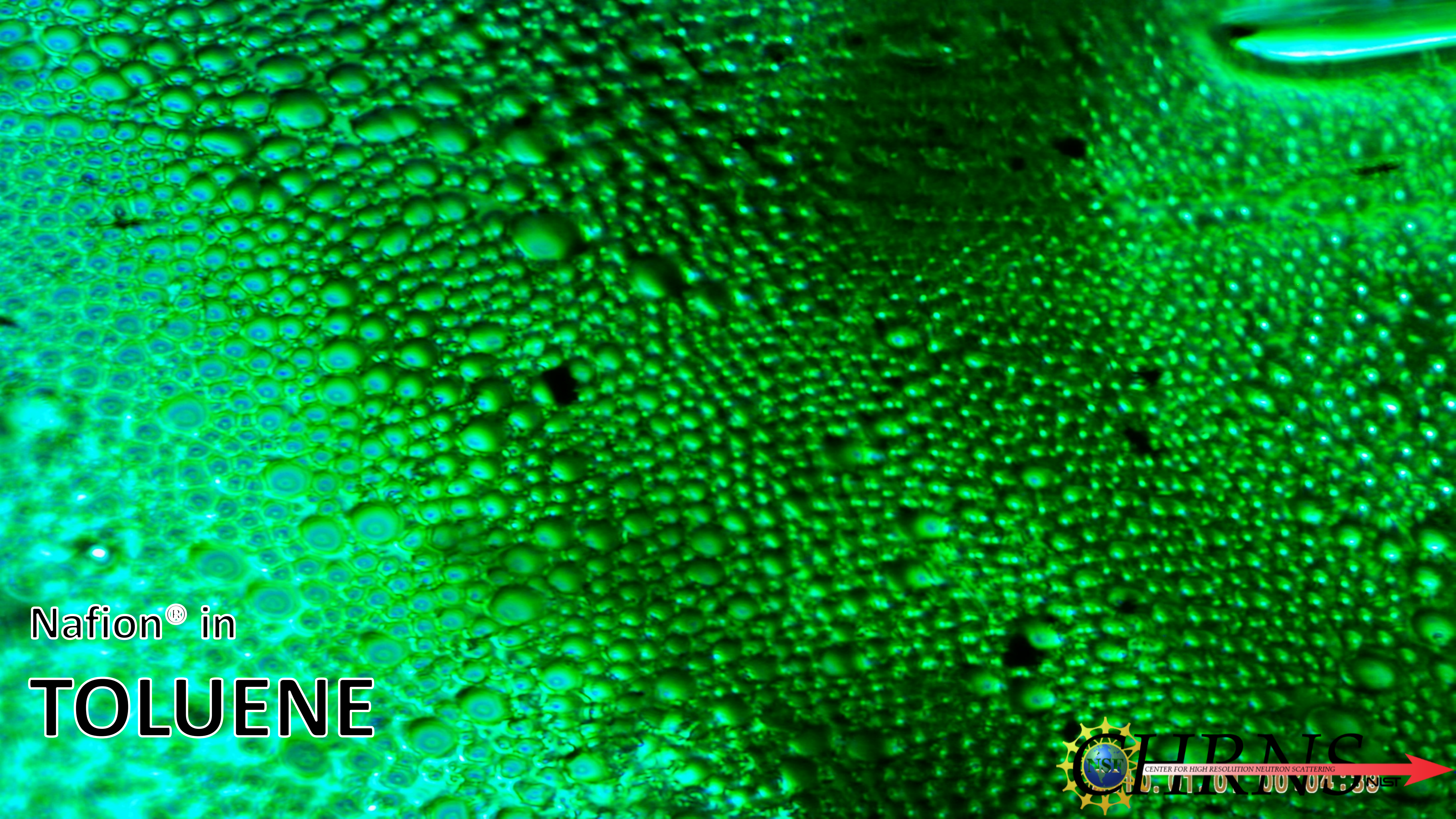
- Assumptions for these models:
  - All excess Nafion® can be cleaned off, leaving only what is attached to SiO_2
  - Relationship between soak time and dips is proportional to Thickness (/Roughness)
  - Relationships are non-linear
    - Soak time model is based on the assumption that as the substrate sits longer, less surface area is available to bond to, and therefore bonding rate will decrease
    - Number of dips model is based on the assumption that each dip removes the excess Nafion® , and that each subsequent dip will remove a set percentage of the loose Nafion® that remains

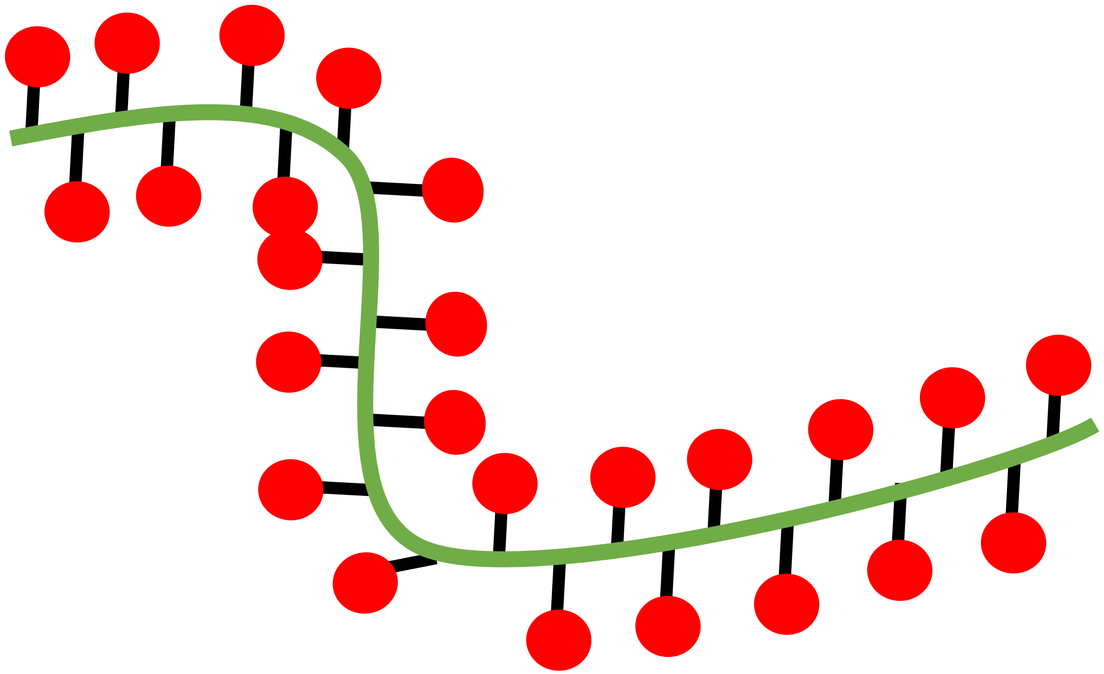


Testing



Solvent Comparison
Vapor Pressure
Polarity Index
250
200
150
100
50
0
0
1
2
3
4
5
6
7
8
9
10
Acetone
Chloroform
THF
Cyclohexane
Ethanol
Toluene
Isopropanol
Water
p-xylene
Chlorobenzene


Nafion® in
TOLUENE
CHRNS
CENTER FOR HIGH RESOLUTION NEUTRON SCATTERING



Objectives

Establish a procedure for ultrathin self-assembled (SA) films over a range of thicknesses that are suitable for NR

Compare interface structures of SA films with those of spin coated films at the nanometer scale

Are there differences induced by shear in the bulk membrane, or at the interface caused by Self-Assembly?

- Thicknesses water uptake etc.
- Explain differences through structure (Ultimately to be found with NR)

Are there separate bonded and entangled layers?

Dead layer/guiselin brush?

Study nature of Nafion binding during SA using a QCM

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NCNR

NSF CHRNS
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NIST